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GEOLOGICAL SURVEY OF ALABAMA
EUGENE ALLEN SMITH, State Geologist

BULLETIN No. 8

THE MATERIALS AND MANUFACTURE OF PORTLAND CEMENT

BY
EDWIN C. ECKEL

THE CEMENT RESOURCES of ALABAMA

BY
EUGENE A. SMITH

GEOLOGICAL SURVEY OF ALABAMA

EUGENE ALLEN SMITH, STATE GEOLOGIST.

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The Materials and Manufacture of Portland Cement.

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EUGENE A. SMITH.

MONTGOMERY, ALABAMA
THE BROWN PRINTING COMPANY, PRINTERS AND BINDERS
1904

To His Excellency, Gov. R. M. Cunningham:

Sir: I have the honor to submit herewith Bulletin No. 8, on the Cement Resources of Alabama; with Preliminary Chapters on the Materials and Manufacture of Portland Cement, by Mr. Edwin C. Eckel, of the United States Geological Survey.

That part of the Report relating specially to the Alabama occurrences was prepared by the writer in coöperation with the United States Geological Survey, and in slightly different form, has been published in Bulletin No. 225, of that Survey. The chapters by Mr. Eckel, which add so much to the value and completeness of the Bulletin, have been generously contributed by him.

Our indebtedness to Senator John T. Morgan is particularly great, since the investigations on which this report is based, were undertaken mainly at his instance, and the coöperation above mentioned, secured through his influence.

Very respectfully,

Eugene A. Smith,
State Geologist.

University of Alabama,
July 1, 1904.

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EOCENE
POST EOCENE
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TUSCALOOSA
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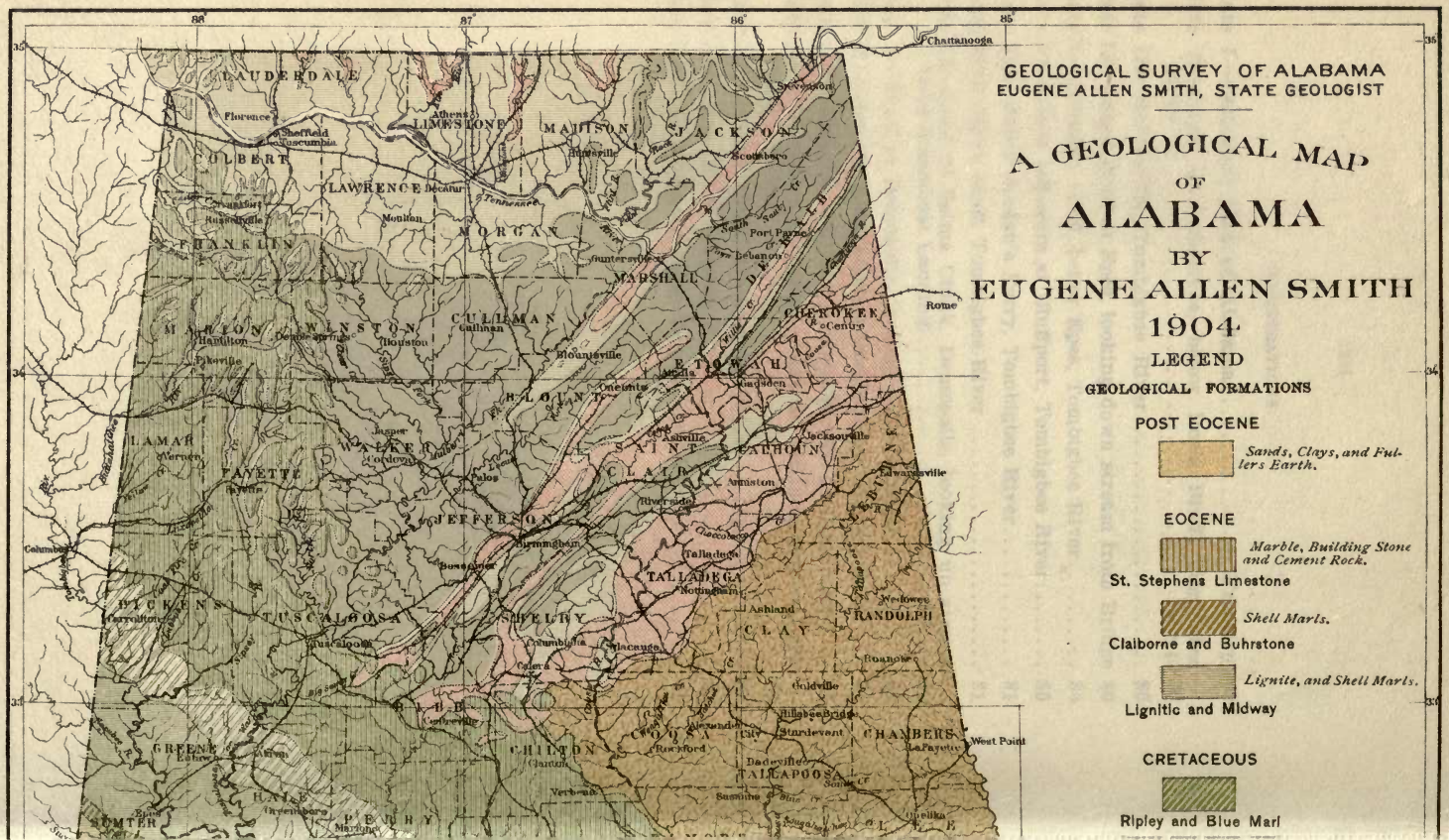
EOCENE VALLEY SOUTH OF ALABAMA
GEOLOGICAL SURVEY OF ALABAMA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LEGEND
GEOLOGICAL FORMATIONS
POST EOCENE
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EOCENE
Marble, Building Stone and Cement Rock.
St. Stephens Limestone
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WINSTON
BLOUNT
ETOWAH
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RANDOLPH
LAMAR
FAYETTE
WALKER
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TALLADEGA
TUSCALOOSA
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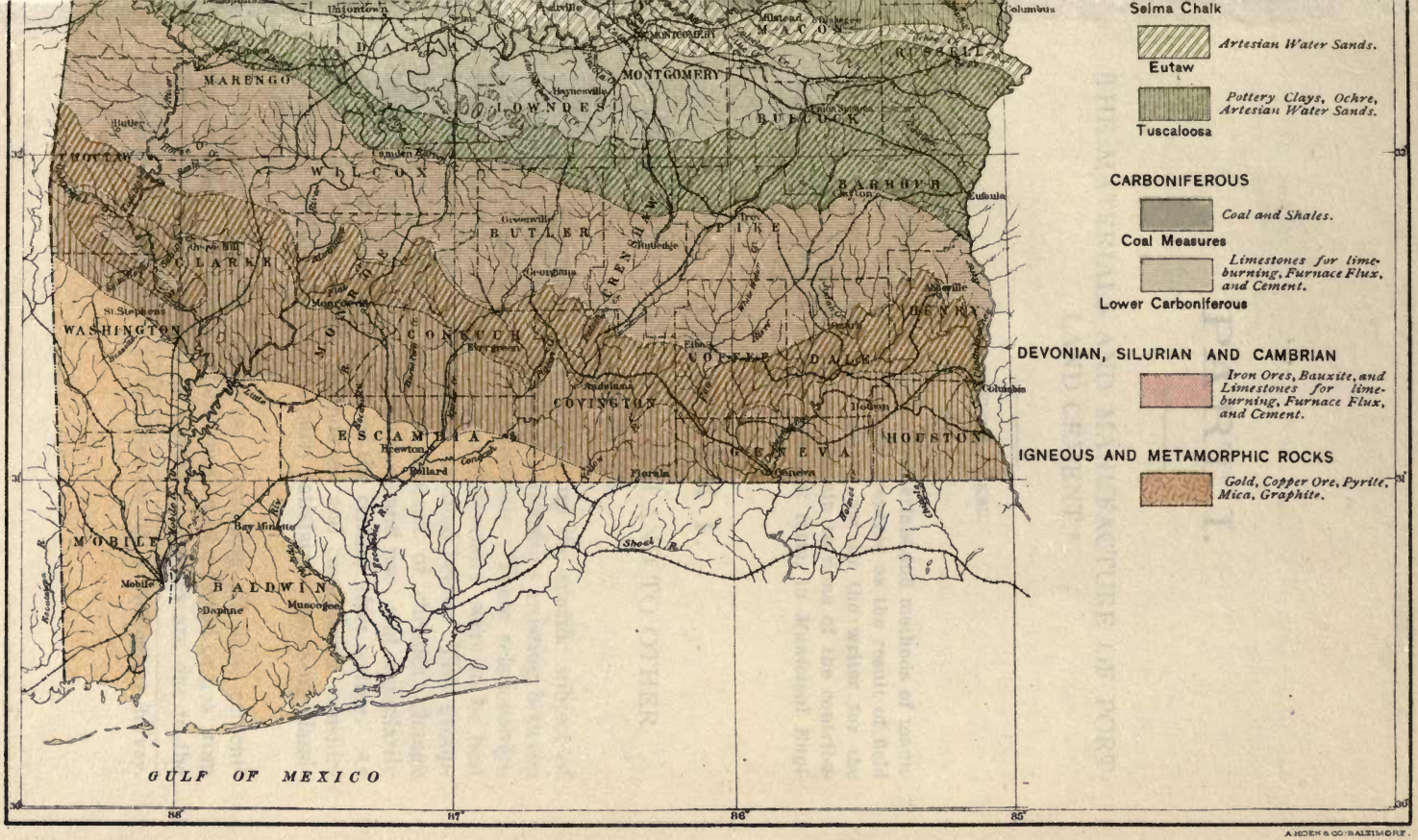

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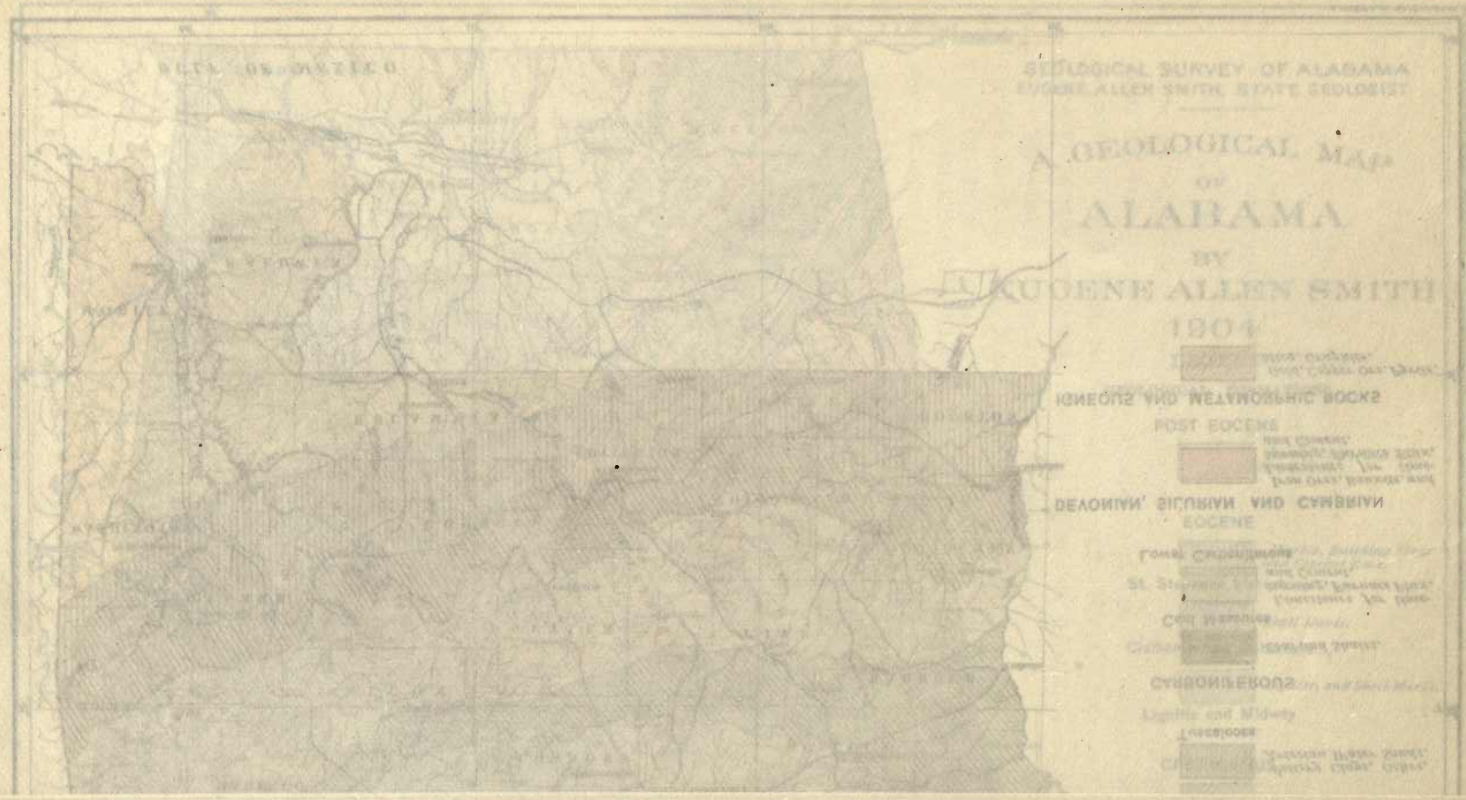
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1894
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EOCENE
CARBONIFEROUS

PART I.

THE MATERIALS AND MANUFACTURE OF PORTLAND CEMENT.*

BY EDWIN C. ECKEL.

[The following paper on the raw materials and methods of manufacture of Portland Cement has been prepared as the result of field work and other investigations carried out by the writer for the United States Geological Survey. Certain sections of the contribution have appeared, in slightly different form, in *Municipal Engineering* during the past two years.]

CHAPTER 1.

THE RELATION OF PORTLAND TO OTHER CEMENTS.

It seems desirable, before taking up the specific subject of Portland cement, to indicate the relationships existing between Portland and other cementing materials. These relationships, both as regards resemblances and differences, seem to be best brought out by the classification presented below. This grouping is based primarily upon the amount of chemical change caused by the process of manufacture and use; and secondarily upon the chemical composition of the cement after setting. As regard is paid to both technologic and commercial considerations, it would seem to be a fairly satisfactory working classification.

GROUP I.—SIMPLE CEMENTS: Including all those cementing materials produced by the expulsion of a liquid or gas from the raw material; and whose setting properties are due to the

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simple reabsorption of the same liquid or gas and the reassumption of original composition; the set cement being therefore similar in composition to the raw material.

Sub-group Ia. Hydrate Cements: Setting properties due to reabsorption of water.

Sub-group Ib. Carbonate Cements: Setting properties due to reabsorption of carbon dioxide.

GROUP II.—COMPLEX CEMENTS: Including all those cementing materials whose setting properties are due to the action of entirely new chemical compounds which were formed during manufacture or use; the set cement being therefore different in composition from the raw material.

Sub-group Ia. Silicate Cements: Setting properties due largely to the formation of silicates.

Sub-group IIb. Oxychloride Cements: Setting properties due to the formation of oxychlorides.

GROUP I—SIMPLE CEMENTS.

The cementing materials included in the present group are those known commercially as "plasters," "hard-finishing cements," and "limes."

The material from which the "plasters" and "hard-finishing cements" are derived is gypsum, a hydrous calcium sulphate; while the limes are derived from limestone, which is essentially calcium carbonate, though usually accompanied by greater or less amounts of magnesium carbonate.

On heating gypsum to a certain temperature, the raw material parts readily with much of its water, leaving an almost anhydrous calcium sulphate, known commercially as plaster-of-Paris. On exposing this plaster to water, it re-hydrates, and again takes the composition of the gypsum from which it was derived.

In like manner limestone, on being sufficiently heated, gives off its carbon dioxide, leaving calcium oxide or "quicklime." This, on exposure to moisture and air carrying carbon dioxide, reabsorbs carbon dioxide and reassumes its original composition, calcium carbonate.

The cementing materials included in this group, therefore,

while differing in composition and properties, agree in certain important points. They are all manufactured by heating a natural raw material sufficiently to remove much or all of its water or carbon dioxide; and, in all, the setting properties of the cementing material are due to the fact that, on exposure to the water or carbon dioxide which has thus been driven off, the cement reabsorbs the previously expelled liquid or gas, and reassumes the chemical composition of the raw material from which it was derived.

Plaster-of-Paris, after setting, is not chemically different from the gypsum from which it was derived; while if the sand, added to avoid shrinkage, be disregarded, hardened lime mortar is nothing more or less than an artificial limestone.

Sub-group Ia. Hydrate Cements.

The materials here included are known in commerce as "plaster-of-Paris," "cement plaster," "Keene's cement," "Parian cement," etc. All of these hydrate cements are based upon one raw material,—gypsum. The partial dehydration of pure gypsum produces plaster-of-Paris. By the addition of gypsum, either by nature or during manufacture, of relatively small amounts of other materials; or by slight variations in the processes of manufacture, the time of setting, hardness, and other important technical properties of the resulting plaster can be changed to a sufficient degree to warrant separate naming and descriptions of the products.

Both the technology and the chemistry of the processes involved in the manufacture of the hydrate cements are simple. The mineral gypsum, when pure, is a hydrous sulphate of lime, of the formula $CaSO_4, 2H_2O$, corresponding to the composition calcium sulphate 79.1%, water 20.9%. Gypsum, as mined, rarely even approximates to this ideal composition, its impurities often amounting to 25% or even more. These impurities, chiefly clayey materials and fragments of quartz and limestone, often exercise an appreciable effect upon the properties of the plaster resulting from burning such impure gypsum.

On burning pure gypsum at a relatively low temperature (350°-400° F.) much of its water of combination is driven off, leaving a partially dehydrated lime sulphate. This, when ground, is plaster of Paris, or if it either naturally or artificial-

ly contains certain impurities, it is called "cement plaster." When either plaster of Paris or cement plaster are mixed with water, the percentage of water which was driven off during calcination is reabsorbed, and the mixture hardens, having again becomes a hydrous sulphate of lime. The processes involved in the manufacture and setting of the dead-burned plasters and hard-finish plasters are slightly more complicated, but the reactions involved are of the same general type.

Sub-group Ib. Carbonate Cements.

The cementing materials falling in the present sub-group are oxides, derived from natural carbonates by the application of heat. On exposure, under proper conditions, to any source of carbon dioxide, the cementing material recorbonates and "sets." In practice the carbon dioxide required for setting is obtained simply by exposure of the mortar to the air. In consequence the set of these carbonate cements, as commonly used, is very slow (owing to the small amount of carbon dioxide which can be taken up from ordinary air); and, what is more important from an engineering point of view, none of the mortar in the interior of a wall ever acquires hardness, as only the exposed portions have an opportunity to absorb carbon dioxide. From the examination of old mortars it has been thought probable that a certain amount of chemical action takes place between the sand and the lime, resulting in the formation of lime silicates; but this effect is slight and of little engineering importance compared with the hardening which occurs in consequence of the reabsorption of carbon dioxide from the air.

Limestone is the natural raw material whose calcination furnishes the cementing materials of this group. If the limestone be an almost pure calcium carbonate it will, on calcination, yield calcium oxide or "quicklime." If, however, the limestone should contain any appreciable percentage of magnesium carbonate, the product will be a mixture of the oxides of calcium and magnesium commercially known as magnesian lime. A brief sketch of the mineralogic relationships of the various kinds of limestone, in connection with the chemistry of lime-burning, will be of service at this point of the discussion.

Pure limestone has the composition of the mineral calcite, whose formula is $CaCO_3$, corresponding to the composition

calcium oxide 56%, carbon dioxide, 44%. In the magnesian limestones part of this calcium carbonate is replaced by magnesium carbonate, the resulting rock therefore having a formula of the type X $CaCO_3$, Y $MgCO_3$. This replacement may reach the point at which the rock has the composition of the mineral dolomite—an equal mixture of the two carbonates, with the formula $CaCO_3$, $MgCO_3$, corresponding to the composition calcium oxide 30.43%, magnesium oxide, 21.74%, carbon dioxide, 47.83%. Limestones may therefore occur with any intermediate amount of magnesium carbonate, and the lime which they produce on calcination will carry corresponding percentages of magnesium oxide, from 0% to 21.74%. Commercially those limes which carry less than 10% of magnesium oxide are, for building purposes, marketable as "pure limes"; while those carrying more than that percentage will show sufficiently different properties to necessitate being marketed as "magnesian limes."

Aside from the question of magnesia, a limestone may contain a greater or lesser amount of impurities. Of these the most important are silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). These impurities, if present in sufficient quantity, will materially affect the properties of the lime produced, as will be noted under the heads of Hydraulic Limes and Natural Cements.

The Carbonate Cements may be divided into two classes:—

(1) High calcium limes;

(2) Magnesian limes.

High Calcium Limes.—On heating a relatively pure carbonate of lime to a sufficiently high degree, its carbon dioxide is driven off, leaving calcium oxide (CaO) or "quicklime." Under ordinary conditions, the expulsion of the carbon dioxide is not perfectly effected until a temperature of 925° C. is reached. The process is greatly facilitated by blowing air through the kiln, or by the injection of steam. On treating quicklime with water, "slacking" occurs, heat being given off, and the hydrated calcium oxide (CaH_2O_2) being formed. The hydrated oxide will, upon exposure to the atmosphere, slowly reabsorb sufficient carbon dioxide to reassume its original composition as lime carbonate. As this reabsorption can take place

only at points where the mortar is exposed to the air, the material in the middle of thick walls never becomes recarbonated. In order to counteract the shrinkage which would otherwise take place during the drying of the mortar, sand is invariably added in the preparation of lime mortars, and as noted above, it is probable that certain reactions take place between the lime and the sand. Such reactions, however, though possibly contributing somewhat to the hardness of old mortars, are only incidental and subsidiary to the principal cause of setting,—recarbonation. The presence of impurities in the original limestone affects the character and value of the lime produced. Of these impurities, the presence of silica and alumina in sufficient quantities will give hydraulic properties to the resulting limes; such materials will be discussed in the next group as Hydraulic Limes and Natural Cements.

Magnesian Limes.—The presence of any considerable amount of magnesium carbonate in the limestone from which a lime is obtained has a noticeable effect upon the character of the product. If burned at the temperature usual for a pure limestone, magnesian limestones give a lime which slakes slowly without evolving much heat, expands less in slaking, and sets more rapidly than pure lime. To this class belongs the well known and much used limes of Canaan (Conn.); Tuckahoe, Pleasantville and Ossining, (N. Y.); various localities in New Jersey and Ohio; Cedar Hollow (Penn.), and Chewacla (Ala.) Under certain conditions of burning, pure magnesian limestone yields hydraulic products, but in this case, as in the case of the product obtained by burning pure magnesite, the set seems to be due to the formation of a hydroxide rather than of a carbonate. Magnesian limestones carrying sufficient silica and alumina will give, on burning, a hydraulic cement falling in the next group under the head of Natural Cements.

GROUP II—COMPLEX CEMENTS.

The cementing materials grouped here as Silicate or Hydraulic Cements, include all those materials whose setting properties are due to the formation of new compounds, during manufacture or use, and not to the mere reassumption of the original composition of the material from which the cement was made. These new compounds may be formed either by chemical change

during manufacture or by chemical interaction, in use, of materials which have merely been mechanically mixed during manufacture.

In the class of silicate cements are included all the materials commonly known as cements by the engineer (natural cements, Portland cement, pozzuolanic cements), together with the hydraulic limes.

Though differing widely in raw material, methods of manufacture and properties, the silicate cements agree in two prominent features: they are all hydraulic (though in very different degrees); and this property of hydraulicity is, in all, due largely or entirely to the formation of tri-calcic silicate ($3\ CaO\ SiO_2$). Other silicates of lime, as well as silico-aluminates, may also be formed; but they are relatively unimportant, except in certain of the natural cements and hydraulic limes where the lime-aluminates may be of greater importance than is here indicated. This will be recurred to in discussing the groups named.

The silicate cements are divisible, on technologic grounds, into four distinct classes. The basis for this division is given below. It will be seen that the first named of these classes (the pozzuolanic cements) differs from the other three very markedly inasmuch as its raw materials are not calcined after mixture; while in the last three classes the raw materials are invariably calcined after mixture. The four classes differ somewhat in composition, but more markedly in methods of manufacture and in the properties of the finished cements.

Classes of Silicate Cements.

1. *Pozzuolanic* Cements*: Produced by the mechanical mixture, without calcination, of slaked lime and a silico-aluminous material (the latter being usually a volcanic ash or blast-furnace slag.)

2. *Hydraulic Limes*: Produced by the calcination, at a temperature not much higher than that of decarbonation, of a siliceous limestone so high in lime carbonate that a considerable amount of free lime appears in the finished product.

---

*Also written Puzzolan.

3. Natural Cements: Produced by the calcination, at a temperature between those of decarbonation and clinkering, of a siliceous limestone (which may also carry notable amounts of alumina and of magnesium carbonate) in which the lime carbonate is so low, relatively to the silica and alumina, that little or no free lime appears in the cement.

4. Portland Cements: Produced by the calcination, at the temperature of semi-vitrefaction ("clinkering") of an artificial mixture of calcareous with silico-aluminous materials, in the proportion of about three parts of lime carbonate to one part of clayey material.

NATURAL CEMENTS.

Natural cements are produced by burning a naturally impure limestone, containing from 15 to 40 per cent. of silica, alumina, and iron oxide. This burning takes place at a comparatively low temperature, about that of ordinary lime burning. The operation can therefore be carried on in a kiln closely resembling an ordinary lime kiln. During the burning the carbon dioxide of the limestone is almost entirely driven off, and the lime combines with the silica, alumina, and iron oxide, forming a mass containing silicates, aluminates, and ferrites of lime. In case the original limestone contained much magnesium carbonate, the burned rock will also contain a corresponding amount of magnesia and magnesian compounds.

After burning, the burned mass will not slack if water be added. It is necessary, therefore, to grind it quite finely. After grinding, if the resulting powder (-natural cement) be mixed with water it will harden rapidly. This hardening or setting will also take place under water. The natural cements differ from ordinary limes in two noticeable ways:

(1) The burned mass does not slack on the addition of water.

(2) After grinding, the powder has hydraulic properties, *i. e.*, if properly prepared, it will set under water.

Natural cements are quite closely related to both hydraulic limes on the one hand, and Portland cement on the other, agreeing with both in the possession of hydraulic properties. They differ from hydraulic limes, however, in that the burned natural cement rock will not slake when water is poured on it.

The natural cements differ from Portland cements in the following important particulars:

(1) Natural cements are not made by burning carefully prepared and finely ground artificial mixtures, but by burning masses of natural rock.

(2) Natural cements, after burning and grinding, are usually yellow to brown in color and light in weight, their specific gravity being about 2.7 to 2.9; while Portland cement is commonly blue to gray in color and heavier, its specific gravity ranging from 3.0 to 3.2.

(3) Natural cements are always burned at a lower temperature than Portland, and commonly at a *much* lower temperature, the mass of rock in the kiln never being heated high enough to even approach the fusing or clinkering point.

(4) In use, natural cements set more rapidly than Portland cement, but do not attain such a high ultimate strength.

(5) In composition, while Portland cement is a definite product whose percentages of lime, silica, alumina and iron oxide vary only between narrow limits, various brands of natural cements will show very great differences in composition.

The material utilized for natural cement manufacture is invariably a clayey limestone, carrying from 13 to 35 per cent. of clayey material, of which 10 to 22 per cent. or so is silica, while alumina and iron oxide together may vary from 4 to 16 per cent. It is the presence of these clayey materials which give the resulting cement its hydraulic properties. Stress is often carelessly or ignorantly laid on the fact that many of our best known natural cements carry large percentages of magnesia, but it should, at this date, be realized that magnesia (*in natural cements at least*) may be regarded as being almost exactly interchangeable with lime, so far as the hydraulic properties of the product are concerned. The presence of magnesium carbonate in a natural cement rock is then merely incidental, while the silica, alumina and iron oxide are essential. The 30 per cent. or so of magnesium carbonate which occurs in the cement rock of the Rosendale District, N. Y., could be replaced by an equal amount of lime carbonate, and the burnt stone would still give a hydraulic product. If, however, the clayey portion (silica, alumina, and iron oxide) of the Rosendale rock could be removed, leaving only the magnesium and lime carbonates, the

burnt rock would lose all of its hydraulic properties and would yield simply a magnesian lime.

This point has been emphasized because many writers on the subject have either explicitly stated or implied that it is the magnesian carbonate of the Rosendale, Akron, Louisville, Utica, and Milwaukee rocks that causes them to yield a natural cement on burning.

PORTLAND CEMENT.

Portland cement is produced by burning a finely ground artificial mixture containing essentially lime, silica, alumina, and iron oxide, in certain definite proportions. Usually this combination is made by mixing limestone or marl with clay or shale, in which case about three times as much of the lime carbonate should be present in the mixture as of the clayey materials. The burning takes place at a high temperature, approaching 3,000° F., and must, therefore, be carried on in kilns of special design and lining. During the burning, combination of the lime with silica, alumina, and iron oxide takes place. The product of the burning is a semi-fused mass called clinker, and consisting of silicates, aluminates, and ferrites of lime in certain definite proportions. This clinker must be finely ground. After such grinding the powder (—Portland cement) will set under water.

As noted above, under the head of Natural Cements, Portland cement is blue to gray in color, with a specific gravity of 3.0 to 3.2, and sets more slowly than natural cements, but soon attains a higher tensile strength.

PUZZOLAN CEMENTS.

The cementing materials included under this name are made by mixing powdered slaked lime with either a volcanic ash or a blast-furnace slag. The product is therefore simply a mechanical mixture of two ingredients, as the mixture is not burned at any stage of the process. After mixing, the mixture is finely ground. The resulting powder (Puzzolan cement) will set under water.

Puzzolan cements are usually light bluish to light yellow in color, and of lower specific gravity and less tensile strength than Portland cement. They are better adapted to use under water than to use in air.

CHAPTER 2.

PORTLAND CEMENT: DEFINITION, COMPOSITION AND CONSTITUTION.

In the following section various possible raw materials for Portland cement manufacture will be taken up, and their relative suitability for such use will be discussed. In order that the statements there made may be clearly understood, it will be necessary to preface this discussion by a brief explanation regarding the composition and constitution of Portland cement.

Use of term Portland.—While there is a general agreement of opinion as to what is understood by the term Portland cement, a few points of importance are still open questions. The definitions of the term given in specifications are in consequence often vague and unsatisfactory.

It is agreed that the cement mixture must consist essentially of lime, silica, and alumina in proportions which can vary but slightly; and that this mixture must be burned at a temperature which will give a semi-fused product—a "clinker." These points must therefore be included in any satisfactory definition. The point regarding which there is a difference of opinion is whether or not cements made by burning a natural rock can be considered true Portlands. The question as to whether the definition of Portland cement should be drawn so as to include or exclude such products is evidently largely a matter of convention; but, unlike most conventional issues, the decision has very important practical consequences. The question at issue may be stated as follows:

If we make artificial mixture of the raw materials and a very high degree of burning the criteria on which to base our definition, we must in consequence of that decision exclude from the class of Portland cements certain well known products, manufactured at several points in France and Belgium by burning a natural rock, without artificial mixture, and at a considerably lower temperature than is attained in ordinary Portland cement practice. These "natural Portlands" of France and Belgium

have always been considered Portland cements by the most critical authorities, though all agree that they are not particularly *high grade* Portlands. So that a definition, based upon the criteria above named, will of necessity exclude from our class of Portland cements some very meritorious products.

There is no doubt that in theory a rock could occur, containing lime, silica, and alumina in such correct proportions as to give a good Portland cement on burning. Actually, however, such a perfect cement rock is of extremely rare occurrence. As above stated, certain brands of French and Belgian "Portland" cements are made from such natural rocks, without the addition of any other material; but these brands are not particularly high grade, and in the better Belgian cements the composition is corrected by the addition of other materials to the cement rock, before burning.

The following definition of Portland cement is of importance because of the large amount of cement which will be accepted annually under the specifications* in which it occurs. It is also of interest as being the nearest approach to an official government definition of the material that we have in this country:

"By a Portland cement is meant the product obtained from the heating or calcining up to incipient fusion of intimate mixtures, either natural or artificial, of argillaceous with calcareous substances, the calcined product to contain at least 1.7 times as much of lime, by weight, as of the materials which give the lime its hydraulic properties, and to be finely pulverized after said calcination, and thereafter additions or substitutions for the purpose only of regulating certain properties of technical importance to be allowable to not exceeding 2 per cent. of the calcined product."

It will be noted that this definition does not require pulverizing or artificial mixing of the materials prior to burning. It seems probable that the Belgian "natural Portlands" were kept in mind when these requirements were omitted. In dealing with American made cements, however,—and the specifications are headed "Specifications for American Portland Cement,"—it is a serious error to omit these requirements. No true Portland cements are at present manufactured in America from natural

*Professional Paper, No. 28, Corps of Engineers, U.S.A., p. 30.

mixtures, without pulverizing and artificially mixing the materials prior to burning. Several plants, however, have placed on the market so-called Portland cements made by grinding up together the underburned and overburned materials formed during the burning of natural cements. Several of these brands contain from 5 to 15 per cent. of magnesia; and under no circumstances can they be considered true Portland cements.

In view of the conditions above noted, the writer believes that the following definition will be found more satisfactory than the above quoted:

Definition of Portland cement.—Portland cement is an artificial product obtained by finely pulverizing the clinker produced by burning to semi-fusion an intimate mixture of finely ground calcareous and argillaceous material, this mixture consisting approximately of one part of silica and alumina to three parts of carbonate of lime (or an equivalent amount of lime oxide.)

Composition and Constitution.—Portland cement may be said to tend toward a composition approximating to pure tricalcic silicate (3 CaO, SiO_2) which would correspond to the proportion CaO 73.6%, SiO_2 26.4%. As can be seen, however, from the published analyses, actual Portland cements as at present made differ in composition very markedly from this. Alumina is always present in considerable quantity, forming with part of the lime, the dicalcic aluminate (2 CaO, SiO_2). This would give, as stated by Newberry, for the general formula of a pure Portland.

$$X\ (3\ CaO,\ SiO_2),\ Y\ (2\ CaO,\ Al_2O_3).$$

But the composition is still further complicated by the presence of accidental impurities, or intentionally added ingredients. These last may be simply adulterants, or they may be added to serve some useful purpose. Calcium sulphate is a type of the latter class. It serves to retard the set of the cement, and, in small quantities, appears to have no injurious effect which would prohibit its use for this purpose. In dome kilns, sufficient sulphur trioxide is generally taken up by the cement from the fuel gases to obviate the necessity for the later addition of calcium sulphate, but in the rotary kiln its addition to the ground cement, in the form of either powdered gypsum or plaster-of-Paris, is a necessity.

Iron oxide, within reasonable limits, seems to act as a substitute for alumina, and the two may be calculated together. Magnesium carbonate is rarely entirely absent from limestones or clays, and magnesia is therefore almost invariably present in the finished cement. Though magnesia, when magnesium carbonate is burned at low temperature, is an active hydraulic material, it does not combine with silica or alumina at the clinkering heat employed in Portland cement manufacture. At the best it is an inert and valueless constituent in the cement; many regard it as positively detrimental in even small amounts, and because of this feeling manufacturers prefer to carry it as low as possible. Newberry has stated that in amounts of less than 3½% it is harmless,—and American Portlands from the Lehigh district usually reach well up toward that limit. In European practice it is carried somewhat lower.

CHAPTER 3.

RAW MATERIALS. GENERAL CONSIDERATIONS.

For the purposes of the present chapter, it will be sufficiently accurate to consider that a Portland cement mixture, when ready for burning, will consist of about 75 per cent. of lime carbonate ($CaCO_3$) and 20 per cent. of silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) together, the remaining 5 per cent. including any magnesium carbonate, sulphur and alkalies that may be present.

The essential elements which enter into this mixture,—lime, silica, alumina and iron,—are all abundantly and widely distributed in nature, occurring in different forms in many kinds of rocks. It can, therefore, be readily seen that, theoretically, a satisfactory Portland cement mixture could be prepared by combining, in an almost infinite number of ways and proportions, many possible raw materials. Obviously, we, too, might expect to find perfect graduations in the *artificialness* of the mixture, varying from the one extreme where a natural rock of absolutely correct composition was used to the other extreme where two or more materials, in nearly equal amounts, are required to make a mixture of correct composition.

The almost infinite number of raw materials which are theoretically available are, however, reduced to a very few in practice under existing commercial conditions. The necessity for making the mixture as cheaply as possible rules out of consideration a large number of materials which would be considered available if chemical composition was the only thing to be taken into account. Some materials otherwise suitable are too scarce; some are too difficult to pulverize. In consequence, a comparatively few combinations of raw materials are actually used in practice.

In certain localities deposits of argillaceous (clayey) limestone or "cement rock" occur, in which the lime, silica, alumina and iron oxide exist in so nearly the proper proportions that only a relatively small amount (say 10 per cent. or so) of other material is required in order to make a mixture of correct composition.

In the majority of plants, however, most or all of the necessary lime is furnished by one raw material, while the silica, alumina and iron oxide are largely or entirely derived from another raw material. The raw material which furnished the lime is usually natural,—a limestone, chalk or marl; but occasionally an artificial product is used, such as the chemically precipitated lime carbonate which results as waste from alkali manufacture. The silica, alumina and iron oxide of the mixture are usually derived from clays, shales or slates; but in a few plants blast-furnace slag is used as the silico-aluminous ingredient in the manufacture of true Portland cement.

The various combinations of raw material which are at present used in the United States in the manufacture of Portland cement may be grouped under six heads. This grouping is as follows:

1. Argillaceous limestone (cement rock) and pure limestone.
2. Pure hard limestone and clay or shale.
3. Soft chalky limestone and clay.
4. Marl and clay.
5. Alkali waste and clay.
6. Slag and limestone.

ORIGIN AND GENERAL CHARACTERS OF LIMESTONE.

The cement materials which are described in the four following sections as argillaceous limestone or cement rock, pure hard limestone, chalk, and marl, though differing sufficiently in their physical and economic characters to be discussed separately and under different names, agree in that they are all forms of limestone. The origin, chemical composition, physical characters, and properties of limestone will, therefore, be briefly taken up in the present chapter to serve as an introduction to the more detailed statements concerning the various types of limestone to be found in the succeeding chapters.

*Origin of limestones.**—Limestones have been formed largely by the accumulation at the sea bottom of the calcareous re-

*For a more detailed discussion of this subject the reader will do well to consult Chapter VIII of Prof. J. F. Kemp's "Handbook of Rocks."

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mains of such organisms as the foraminifera, corals, and mollusks. Most of the thick and extensive limestone deposits of the United States were probably deep-sea deposits formed in this way. Many of these limestones still show the fossils of which they were formed, but in others all trace of organic origin has been destroyed by the fine grinding to which the shells and corals were subjected before their deposition at the sea-bottom. It is probable also that part of the calcium carbonate of these limestones was a purely chemical deposit from solution, cementing the shell fragments together.

A far less extensive class of limestones—though important in the present connection—owe their origin to the indirect action of organisms. The "marls," so important today as Portland cement materials, fall in this class. As the class is of limited extent, however, its method of origin may be dismissed here, but will be described later in the section on Marls.

Deposition from solution by purely chemical means has unsdoubtedly given rise to numerous limestone deposits. When this deposition took place in caverns or in the open air, it gave rise to onyx deposits and to the "travertine marls" of certain Ohio and other localities; when it took place in isolated portions of the sea through the evaporation of the sea water it gave rise to the limestone beds which so frequently accompany deposits of salt and gypsum.

Varieties of limestone.—A number of terms are in general use for the different varieties of limestone, based upon differences of origin, texture, composition, etc. The more important of these terms will be briefly defined.

The *marbles* are limestones which, through the action of heat and pressure, have become more or less distinctively crystalline. The term *marl*, as at present used in cement manufacture, is applied to a loosely cemented mass of lime carbonate formed in lake basins as described on a later page. *Calcareous tufa* and *travertine* are more or less compact limestones deposited by spring or stream waters along their courses. *Oolitic* limestones, so called because of their their resemblance to a mass of fish-roe, are made up of small rounded grains of lime carbonate. *Chalk* is a fine-grained limestone composed of finely comminuted shells, particularly those of the foraminifera. The presence of much silica gives rise to a *siliceous* or *cherty* limestone. If the

silica present is in combination with alumina, the resulting limestone will be *clayey* or *argillaceous*.

Chemical composition of limestone—A theoretically pure limestone is merely a massive form of the mineral calcite. Such an ideal limestone would therefore consist entirely of calcium carbonate or carbonate of lime, with the formula $CaCO_3$ ($CaO+CO_2$), corresponding to the composition calcium oxide (CaO) 56 per cent.; carbon dioxide or carbonic acid (CO_2) 44 per cent.

As might be expected, the limestones we have to deal with in practice depart more or less widely from this theoretical composition. These departures from ideal purity may take place along either of two lines,—

a. The presence of magnesia in place of part of the lime;

b. The presence of silica, iron, alumina, alkalies, or other impurities.

It seems advisable to discriminate between these two cases, even though a given sample of limestone may fall under both heads, and they will therefore be discussed separately.

a. *The presence of magnesia in place of part of the lime.*—The theoretically pure limestones are, as above noted, composed entirely of calcium carbonate and correspond to the chemical formula $CaCO_3$. Setting aside for the moment the question of the presence or absence of such impurities as iron, alumina, silica, etc., it may be said that lime is rarely the only base in a limestone. During or after the formation of the limestone a certain percentage of magnesia is usually introduced in place of part of the lime, htus giving a more or less magnesian limestone. In the magnesian limestones part of this calcium carbonate is replaced by magnesium carbonate ($Mg\ CO_3$), the general formula for a magnesian limestone being therefore

$$x\ Ca\ CO_3 + y\ Mg\ CO_3.$$

In this formula x may vary from 100% to zero, while y will vary inversely from zero to 100%. In the particular case of this replacement where the two carbonates are united in equal *molecular* proportions, the resultant rock is called dolomite. It has the formula,—$CaCO_3$, $MgCO_3$—corresponding to the composition calcium carbonate 54.35 per cent.; magnesium carbonate 45.65 per cent. In the case where the calcium carbonate has been entirely replaced by magnesium carbonate, the resulting

pure carbonate of magnesia is called magnesite, having the formula $MgCO_3$ and the composition magnesia (MgO) 47.6 per cent.; carbon dioxide (CO_2), 52.4 per cent.

Rocks of this series may therefore vary in composition from pure calcite-limestones at one end of the series to pure magnesite at the other. The term limestone has, however, been restricted in general use to that part of the series lying in composition between calcite and dolomite, while all those more uncommon phases carrying more magnesium carbonate than the 45.65 per cent. of dolomite are usually described simply as impure magnesites.

The presence of much magnesia in the finished cement is considered undesirable, 3½ per cent. being the maximum permissible under most specifications, and therefore the limestone to be used in Portland cement manufacture should carry not over 5 to 6 per cent. of magnesium carbonate.

Though magnesia is often described as an "impurity" in limestone, this word, as can be seen from the preceding statements, hardly expresses the facts in the case. The magnesium carbonate present, whatever its amount, simply serves to replace an equivalent amount of calcium carbonate, and the resulting rock, whether little or much magnesia is present, is still a pure carbonate rock. With the impurities to be discussed in later paragraphs, however, this is not the case. Silica, alumina, iron, sulphur, alkalies, etc., when present, are actual impurities, not merely chemical replacements of part of the calcium carbonate.

b. *The presence of silica, iron, alumina, alkalies, and other impurities.*—Whether a limestone consists of pure calcium carbonate or more or less of magnesium carbonate, it may also contain a greater or lesser amount of distinct impurities. From the point of view of the cement manufacturer, the more importan of these impurities are silica, alumina, iron, alkalies, and sulphur, all of which have a marked effect on the value of the limestone as a cement material. These impurities will therefore be taken up in the order in which they are named above.

The silica in a limestone may occur either in combination with alumina, as a clayey impurity, or not combined with alumina. As the effect on the value of the limestone would be very different in the two cases, they will be taken up separately.

Silica alone.—Silica, when present in a limestone containing no alumina, may occur in one of three forms, and the form in

which it occurs is of great importance in connection with cement manufacture.

(1) In perhaps its commonest form, silica is present in nodules, masses or beds of flint or chert. Silica occurring in this form will not readily enter into combination with the lime of a cement mixture, and a cherty or flinty limestone is therefore almost useless in cement manufacture.

(2) In a few cases, as in the hydraulic limestone of Teil, France, a large amount of silica is present and very little alumina; notwithstanding which the silica readily combines with the lime on burning. It is probable that in such cases the silica is present in the limestone in a very finely divided condition, or possibly as hydrated silica, possibly as the result of chemical precipitation or of organic action. In the majority of cases, however, a highly siliceous limestone will not make a cement on burning unless it contains alumina in addition to the silica.

(3) In the crystalline limestone (marbles) and less commonly in uncrystalline limestones, whatever silica is present may occur as a complex silicate in the form of shreds of mica, hornblende, or other silicate mineral. In this form silicate is somewhat intractable in the kiln, and mica and other silicate minerals are therefore to be regarded as inert and useless impurities in a cement rock. These silicates will flux at a lower temperature than pure silica and are thus not so troublesome as flint or chert. They are, however, much less serviceable than if the same amount of silica were present in combination with alumina as a clay.

Silica with alumina.—Silica and alumina, combined in the form of clay, are common impurities in limestone, and are of special interest to the cement manufacturer. The best known example of such an argillaceous limestone is the cement rock of the Lehigh district of Pennsylvania. Silica and alumina, when present in this combined form, combine readily with the lime under the action of heat, and an argillaceous limestone therefore forms an excellent basis for a Portland cement mixture.

Iron.—Iron when present in a limestone occurs commonly as the oxide (Fe_2O_3), or sulphide (FeS_2); more rarely as iron carbonate or in a complex silicate. Iron in the oxide, carbonate or silicate form, is a useful flux, aiding in the combination of the

lime and silica in the kiln. When present as a sulphide, in the form of the mineral pyrite it is to be avoided in quantities over 2 or 3 per cent.

Physical characters of limestones.—In texture, hardness, and compactness, the limestones vary from the loosely consolidated marls through the chalks to the hard compact limestones and marbles. Parallel with these variations are variations in absorptive properties and density. The chalky limestones may run as low in specific gravity as 1.85, corresponding to a weight of say 110 pounds per cubif oot, while the compact limestones commonly used for building purposes range in specific gravity between 2.3 and 2.9, corresponding approximately to a range in weight of from 140 to 185 pounds per cubic foot.

From the point of view of the Portland cement manufacturer, these variations in physical properties are of economic interest chiefly in their bearing upon two points: the percentage of water carried by the limestone as quarried, and the ease with which the rock may be crushed and pulverized. To some extent the two properties counterbalance each other; the softer the limestone the more absorbent is it likely to be. These purely economic features will be discussed in more detail in later chapters.

Effect of heating on limestone.—On heating a non-magnesian limestone to or above 300° C., its carbon dioxide will be driven off, leaving quicklime (calcium oxide, CaO). If a magnesian limestone be similarly treated, the product would be a mixture of calcium oxide and magnesium oxide (MgO). The rapidity and perfection of this decomposition can be increased by passing steam or air through the burning mass. In practice this is accomplished either by the direct injection of air or steam, or more simply by thoroughly wetting the limestone before putting it into the kiln.

If, however, the limestone contains an appreciable amount of silica, alumina and iron, the effects of heat will not be of so simple a character. At temperature of 800° C. and upwards these clayey impurities will combine with the lime oxide, giving silicates, aluminates and related salts of lime. In this manner a natural cement will be produced. An artificial mixture of certain and uniform composition, burned at a higher temperature, will give a Portland cement, the details of whose manufacture are discussed on later pages.

CHAPTER 4.

RAW MATERIALS IN DETAIL.

Argillaceous Limestone: Cement Rock.

An argillaceous limestone containing approximately 75 per cent. of lime carbonate and 20 per cent. of clayey materials (silica, alumina, and iron oxide), would, of course, be the ideal material for use in the manufacture of Portland cement, as such rock would contain within itself in the proper proportions all the ingredients necessary for the manufacture of a good Portland. It would require the addition of no other material, but when burnt alone would give a good cement. This ideal cement material is, of course, never realized in practice, but certain deposits of argillaceous limestone approach the ideal composition very closely.

The most important of these argillaceous limestone or "cement rock" deposits is, at present, that which is so extensively utilized in Portland cement manufacture in the "Lehigh district" of Pennsylvania and New Jersey. As this area still furnishes about two-thirds of all the Portland cement manufactured in the United States, its raw materials will be described in some detail.

Cement rock of the Lehigh district.—The Lehigh district of the cement trade comprises parts of Berks, Lehigh, and Northampton counties, Pennsylvania, and of Warren county, New Jersey. Within this relatively small area about twenty Portland cement mills are located, producing slightly over two-thirds of the entire American output. As deposits of the cement rock used by these plants extend far beyond the present "Lehigh district," a marked extension of the district will probably take place as the needs for larger supplies of raw material becomes more apparent.

The "cement rock" of the Lehigh district is a highly argillaceous limestone of Trenton (Lower Silurian) age. The formation is about 300 feet in thickness in this area. The rock is a very dark gray in color and usually has a slaty fracture. In composition it ranges from about 60 per cent. lime carbonate

with 30 per cent. of clayey material, up to say 80 per cent. lime carbonate with 15 per cent. of silica, alumina and iron. The lower beds of the formation are always higher in lime carbonate than are the beds nearer the top of the formation. The content of magnesium carbonate in these cement rocks is always high, (as Portland cement materials go), ranging from 3 to 6 per cent.

Near, and in some cases immediately underlying these cement beds, are beds of purer limestone ranging from 85 to 96 per cent. lime carbonate. The usual practice in the Pennsylvania and New Jersey plants has been therefore to mix a relatively small amount of this purer limestone with the low lime "cement rock" in such proportions as to give a cement mixture of proper composition.

The economic and technologic advantages of using such a combination of materials are very evident. Both the pure limestone and the cement rock, particularly the latter, can be quarried very easily and cheaply. As quarried they carry but little water so that the expense of dryidg them is slight. The fact that about four-fifths of the cement mixture will be made up of a natural cement rock permits coarser granding of the raw mixture than would be permissible in plants using pure limestone or marl with clay. This point is more fully explained on a later page. It seems probable, also, that when using a natural cement rock as part of the mixture the amount of fuel necessary to clinker the mixture is less than when pure limestone is mixed with clay.

Such mixtures of argillaceous limestone or "cement rock" with a small amount of pure limestone evidently possess important advantages over mixtures of pure hard limestone or marl with clay. They are, on the other hand, less advantageous as cement materials than the chalky limestones discussed on later pages.

The analyses in Table 2 are fairly representative of the materials employed in the Lehigh district. The first four analyses are of "cement rock"; the last two are of the purer limestone used for mixing with it.

Analyses of Lehigh district cement materials.

	Cement rock				Limestone	
Silica (SiO_2)	10.02	9.52	14.52	16.10	3.02	1.98
Alumina (Al_2O_3)	6.26	4.72	6.52	2.20	1.90	0.70
Iron Oxide (Fe_2O_3) ...						
Lime carbonate ($CaCO_3$)..	78.65	80.71	73.52	76.23	92.05	95.15
Magnesium carbonate ($MgCO_3$)	4.71	4.92	4.69	3.54	3.04	2.03

"Cement rock" in other parts of the United States.—Certain Portland cement plants, particularly in the western United States, are using combinations of materials closely similar to those in the Lehigh district. Analyses of the materials used at several of these plants are given in Table III.

Analyses of "cement rock" materials from the western United States.

	Utah.		California		Colorado	
	Cement rock	Limestone	Cement rock	Limestone	Cement rock	Limestone
Silica (SiO_2)	21.2	6.8	20.06	7.12	14.20	
Alumina (Al_2O_3)	8.0	3.0	10.07	2.36	5.21	
Iron Oxide (Fe_2O_3)			3.39	1.16	1.73	
Lime carbonate ($CaCO_3$)...	62.08	89.8	63.40	87.70	75.10	88.0
Magnesium carbonate ($MgCO_3$)	3.8	0.76	1.54	0.84	1.10	

In addition to the "cement rocks" noted in this chapter, it is necessary to call attention to the fact that many of the chalky limestones discussed on page 26 are sufficiently argillace-

ous to be classed as 'cement rocks." Because of their softness, however, all the chalky limestones will be described together.

Pure hard limestones.

Soon after the American Portland cement industry had become fairly well established in the Lehigh district, attempts were made in New York State to manufacture Portland cement from a mixture of pure limestone and clay. These attempts were not commercially successful, and although their lack of success was not due to any defects in the limestone used, a certain prejudice arose against the use of the hard limestones. In recent years, however, this has disappeared, and a very large proportion of the American output is now made from mixtures of limestone with clay or shale. (See page 21 for comparative figures.) This reëstablishment in favor of the hard limestones is doubtless due, in great part, to recent improvements in grinding machinery, for the purer limestones are usually much harder than argillaceous limestones like the Lehigh district "cement rock," and it was very difficult to pulverize them finely and cheaply with the crushing appliances in use when the Portland cement industry was first started in America.

A series of analyses of representative pure hard limestones, together with analyses of the clays or shales with which they are mixed, is given in the table.

Analyses of pure hard limestones and clayey materials.

	Limestones.			
Silica (SiO_2)	1.72	0.86	0.56	0.40
Alumina (Al_2O_2)	1.63	0.63	1.23	0.44
Iron oxide (Fe_2O_3)	6.59	1.03	0.29	
Lime carbonate ($CaCO_3$)	90.58	97.06	97.23	97.99
Magnesium carbonate ($MgCO_3$)	....	....	0.75	0.42
	Clays and Shales.			
Silica (SiO_2)	63.56	55.80	56.30	60.00
Alumina (Al_2O_2)	27.32	30.20	29.86	23.36
Iron oxide (Fe_2O_3)				4.32
Lime carbonate ($CaCO_3$)	3.60	2.54	....	1.70
Magnesium carbonate ($MgCO_3$)	2.60	....	....	1.50

The first limestone analysis given in the above table represents a curious type, used in several plants in the Middle West. As will be noted, it is a relatively impure limestone, but its principal impurity is iron oxide. It contains 8.22 per cent. of iron oxide and alumina, as compared with 1.72 per cent. of silica: and therefore demands great care in the selection of a suitable high-silica clay to mix with it.

Soft Limestones: Chalk.

Origin and general character.—Chalk, properly speaking, is a pure carbonate of lime composed of the remains of the shells of minute organisms, among which those of foraminifere are especially prominent. The chalks and soft limestones discussed in this chapter agree, not only in having usually originated in this way, but also in being rather soft and therefore readily and cheaply crushed and pulverized. As Portland cement materials they are, therefore, almost ideal. One defect, however, which to a small extent counterbalances their obvious advantages is the fact that most of these soft, chalky limestones absorb water quite readily. A chalky limestone which in a dry season will not carry over 2 per cent. of moisture as quarried, may, in consequence of prolonged wet weather show as high as 15 or 20 per cent. of water. This difficulty can, of course, be avoided if care be taken in quarrying to avoid unnecessary exposure to water and, if necessary, to provide facilities for storing a supply of the raw materials during wet seasons.

Geographic and geologic distribution in the United States.—The chalks and chalky limestones are confined almost entirely to certain southern and western States. They are all of approximately the same geologic ages,—Cretaceous or Tertiary,—and are mostly confined to one division of the Cretaceous. The principal chalk or soft limestone deposits available for use in Portland cement manufacture occur in three widely separated areas, occupying respectively (*a*) parts of Alabama and Mississippi; (*b*) parts of Texas and Arkansas; and, (*c*) parts of Iowa, Nebraska, North and South Dakota.

Composition.—In composition these chalks, or "rotten limestones," vary from a rather pure calcium carbonate, low in both magnesia and clayey materials, to an impure clayey limestone, requiring little additional clay to make it fit for use in Portland cement manufacture. Analyses quoted from various authors of a number of these chalky limestones are given in Table IV, and will serve to show their range of composition.

Analyses of Chalky Limestones.

	Demopolis, Ala.	San Antonio, Texas.	Dallas, Texas.	White Cliffs, Ark.	Yankton, S. Dak.	Milton, N. Dak.
Silica	12.13	5.77	23.55	7.97	8.20	9.15
Alumina	4.17	}				} 4.80
Iron oxide	3.28	} 2.12	1.50	1.09	7.07	} 2.30
Lime carbonate ..	75.07	90.15	70.21	88.64	83.59	63.75
Magnesium carb'te	.92	.15	.58	.73	n.d.	1.25

Fresh-Water Marls.

Marls, in the sense in which the term is used in the Portland cement industry, are incoherent limestones which have been deposited in the basins of existing or extinct lakes. So far as chemical composition is concerned, marls are practically pure limestones, being composed entirely of calcium carbonate. Physically, however, they differ greatly from the compact rocks which are commonly described as limestones, for the marls are granular, incoherent deposits. This curious physical character of marls is due to the conditions under which they have been deposited, and varies somewhat according to the particular conditions which governed their deposition in different localities.

A warning to the reader concerning other uses of the term "marl" may profitably be introduced here. The meaning above given is that in which the term marl is commonly used in the cement industry at the present day. But in geological and agricultural reports, particularly in those issued before the Port-

land cement industry became prominent in this country, the term marl has been used to cover several very different substances. The following three uses of the term will be found particularly common, and must be guarded against when such reports are being examined in search for descriptions of deposits of cement materials.

(1.) In early days the term "marls" and "marlytes" were used to describe deposits of calcareous shales—and often covered shales which were not particularly calcareous. This use of the term will be found in many of the earlier geological reports issued by New York, Ohio, and other interior States.

(2.) In New Jersey and the States southward bordering on the Atlantic and Gulf of Mexico, the term marl is commonly applied to deposits of soft chalky or unconsolidated limestone, often containing considerable clayey and phosphatic matter. These limestones are of marine origin, and not related to the fresh-water marl deposits which are the subject of the present chapter.

(3.) In the same States as are included in the last paragraph, but particularly in New Jersey and Virginia, large deposits of the so-called 'green sand marls" occur. This material is, in no way, related to the true marls (which are essentially lime carbonates), but consists almost entirely of an iron silicate, with very small percentages of clayey, calcareous, and phosphatic matter.

Origin or marls.—The exact cause of the deposition of marls has been the subject of much investigation and discussion, particularly in the past few years, since they have become of economic importance. The reader who wishes to obtain further details concerning this question will do well to refer to the following series of papers.

(1.) Blatchley, W. S., and Ashley, G. H. The Lakes of Northern Indiana, and their associated marl deposits, in 25th Ann. Rept. Indiana Dept. Geology and Natural Resources, pp. 31-321.

(2.) Davis, C. A. A contribution to the natural history of marl. Journal of Geology, Vol. 8, pp. 485-497.

(3.) Davis, C. A. Second contribution to the natural history of marl. Journal of Geology, Vol. 9, pp. 491-506.

(4.) Davis, C. A. A contribution to the natural history of marl. Vol. 8, pt. 3, Reports Michigan Geological Survey, pp. 65-102.

(5.) Lane, A. C. Notes on the origin of Michigan bog limes. Vol. 8, pt. 3, Reports Michigan Geological Survey, pp. 199-223.

Disregarding the points in controversy, which are of no particular practical importance, it may be said that marls are deposited in lakes by spring or stream waters carrying lime carbonate in solution. The actual deposition is in part due to purely physical and chemical causes, and in part to the direct or indirect action of animal or vegetable life. The result, in any case, is that a calcareous deposit forms along the sides and over the bottom of the lake, this deposit consisting of lime carbonate, mostly in a finely granular form, interspersed with shells and shell fragments.

Geographic distribution of marl deposits.—The geographic distribution of marl deposits is intimately related to the geologic history of the region in which they occur. Marl-beds are, as indicated in the preceding section, the result of the filling of lake basins. Lakes are not common except in those portions of the United States which were affected by glacial action, since lakes are in general due to the damming of streams by glacial material. Workable marl deposits, therefore, are almost exclusively confined to those portions of the United States and Canada lying north of the former southern limit of the glaciers.

Marl beds are found in the New England States, where they are seldom of important size, and in New York, where large beds occur in the central and western portions of the State. Deposits are frequent and important in Michigan, and in the northern portions of Ohio, Indiana, and Illinois. Marl beds occur in Wisconsin and Minnesota, but have not been as yet exploited for cement manufacture.

Composition.—As shown by the analyses below, marls are usually very pure lime carbonates. They, therefore, require the addition of considerable clay to bring them up to the proper composition for a Portland cement mixture.

The marls are readily excavated, but necessarily carry a large percentage of water. The mixture, on this account, is commonly made in the wet way, which necessitates driving off a high percentage of water in the kilns. Analyses of typical marls and clays are given in the following table.

Analyses of marls and clays used in cement plants.

	Marl.			Clay.		
Silica	0.25	3.0	1.60	40.48	52.0	63.75
Alumina	}				} 17.0	16.40
Iron oxide	} .10		1.55	20.95	} 5.0	6.35
Lime carbonate ...	94.39	93.0	88.9	25.80	20.0	4.0
Magnesium carb'te	.38	1.5	.94	.99	....	2.1

Alkali Waste.

A very large amount of waste material results from the process used at alkali works in the manufacture of caustic soda. This waste material is largely a precipitated form of calcium carbonate, and if it is sufficiently free from impurities, it furnishes a cheap source of lime for use in Portland cement manufacture.

The availability of alkali waste for this purpose depends largely on what process was used at the alkali plant. Leblanc process waste, for example, carries a very large percentage of sulphides, which prevents its use as a Portland cement material. Waste resulting from the use of the ammonia process, on the other hand, is usually a very pure mass of lime, mostly in the form of carbonate, though a little lime hydrate is commonly also present. As pyrite is not used in the ammonia process, its waste is usually low enough in sulphur to be used as a cement material. The waste may carry a low or a very high percentage of magnesia, according to the character of the limestone that has been used. When a low-magnesia limestone has been used, the resulting was te is a very satisfactory Portland cement material.

The following analyses are fairly representative of the waste obtained at alkali plants using the ammonia process.

Analyses of alkali waste.

	1	2	3	4
Silica (SiO_2)	0.60	1.75	1.98	0.98
Alumina (Al_2O_3)	3.04	0.61	1.41	1.62
Iron oxide (Fe_2O_3)			1.38	
Lime (CaO)	53.33	50.60	48.29	50.44
Magnesia (MgO)	0.48	5.35	1.51	4.97
Alkalies (Na_2O, K_2O)	0.20	0.64	0.64	0.50
Sulphur trioxide (Co_3)	n.d.	n.d.	1.26	n.d.
Sulphur (S)	n.d.	0.10	n.d.	0.06
Carbon dioxide (CO_2)	42.43		39.60	n.d.
Water and organic matter	n.d.	41.70	3.80	n.d.

Of the analyses quoted in the preceding table, those in the first and third columns represent materials which are actually used in Portland cement manufacture in England and the United States. The alkali wastes whose analyses are given in the second and fourth columns are notably too high in magnesia to be advisable for such use.

Blast furnace slag.

True Portland cements, which must be sharply distinguished from the slag (or puzzolan) cements can be made from mixtures which contain blast furnace slag as one ingredient. In this case the slag is intimately mixed with limestone and the mixture is finely powdered. It is then burned in kilns and the resulting clinker pulverized.

The slags from iron furnaces consist essentially of lime (CaO), silica (SiO_2), and alumina (Al_2O_3); though small percentages of iron oxide (FeO), magnesia (MgO), and sulphur (S), are commonly present. Slag may therefore be regarded as a very impure limestone or a very calcareous clay.

The slag used at a German Portland cement plant has the following range in composition.

Analysis of slag used in Portland cement manufacture.

Silicia (SiO_2)	30.	35.
Alumina (Al_2O_3)	10.	14.
Iron oxide (FeO)	0.2	1.2
Lime (CaO)	46.	49.
Magnesia (MgO)	0.5	3.5
Sulphur trioxide (SO_3)	0.2	0.6

Clays and Shales.

Clays are ultimately derived from the decay of older rocks, the finer particles resulting from this decay being carried off and deposited by streams along their channels, in lakes, or along parts of the sea coast or sea bottom as beds of clay. In chemical composition the clays are composed essentially of silica and alumina, though iron oxide is almost invariably present in more or less amount, while lime, magnesia, alkalies and sulphur are of frequent occurrence, though usually only in small percentages.

Shales are clays which have become hardened by pressure. The so-called "fire-clays" of the Coal Measures are shales, as are many of the other "clays" of commerce.

For use as Portland cement materials clays or shales should be as free as possible from gravel and sand, as the silica present as pebbles or grit is practically inert in the kiln unless ground more finely than is economically practicable. In composition they should not carry less than 55 per cent. of silica, and preferably from 60 to 70 per cent. The alumina and iron oxide together should not amount to more than one-half the percentage of silica, and the composition will usually be better the nearer the ratio $\frac{Al_2O_3+Fe_2O_3}{3}=SiO_2$ is approached.

Nodules of lime carbonate, gypsum or pyrite, if present in any quantity, are undesirable; though the lime carbonate is not absolutely injurious. Magnesia and alkalis should be low, preferably not above 3 per cent.

Analyses of clays and shales used in various American Portland cement plants will be found on pages 27 and 30.

Slate.

Slate is, so far as origin is concerned, merely a form of shale in which a fine, even and parallel cleavage has been developed by pressure. In composition, therefore, it will vary exactly as do the shales considered on previous pages, and so far as composition alone is concerned, slate would not be worthy of more attention, as a Portland cement material, than any other shale.

Commercial considerations in connection with the slate industry, however, make slate a very important possible source of cement material. Good roofing slate is a relatively scarce material, and commands a good price when found. In the preparation of roofing slate for the market so much material is lost during sawing, splitting, etc., that only about 10 to 25 per cent. of the amount quarried is salable as slate. The remaining 75 to 90 per cent. is of no service to the slate miner. It is sent to the dump heap, and is a continual source of trouble and expense. This very material, however, as can be seen from the analyses quoted below, is often admirable for use, in connection with limestone, in a Portland cement mixture. As it is a waste product, it could be obtained very cheaply by the cement manufacturer.

Composition of American roofing slates.

	Max.	Average	Min.
Silica (SiO_2)	68.62	60.64	54.05
Alumina (Al_2O_3)	24.71	18.05	9.77
Iron oxides (FeO, Fe_2O_3)	10.66	6.87	2.18
Lime (CaO)	5.23	1.54	....
Magnesia (MgO)	6.43	2.60	0.12
Alkalies (K_2O, Na_2O)	8.68	4.74	1.93
Ferrous sulphide (FeS_2)	....	0.38	....
Carbon dioxide (CO_2)	....	1.47	....
Water of combination	....	3.51	....
Moisture, below 110°C.	....	0.62	....

CHAPTER 5.

ECONOMIC CONSIDERATIONS AND METHODS OF MANUFACTURE.

Determining the possible value for Portland cement manufacture of a deposit of raw material is a complex problem, depending upon a number of distinct factors, all of which must be given due consideration. The more important of these factors are:

(1.) Chemical composition of the material.
(2.) Physical character of the material.
(3.) Amount of material available.
(4.) Location of the deposit with respect to transportation routes.
(5.) Location of the deposit with respect to fuel supplies.
(6.) Location of the deposit with respect to markets.

The natural raw materials used at present in Portland cement manufacture are obtained by one of three methods,—(a) quarrying; (b) mining, and (c) dredging. When the cement manufacturer is given an opportunity to choose between these different methods of excavation, his choice will depend partly on the physical character of the material to be excavated and partly on the topographical and geological conditions. Usually, however, there is no opportunity for a choice of methods, for in any given case one of the methods will be so evidently the only possible mode of handling the material as to leave no room for other considerations.

The three different methods of excavation will first be briefly considered, after which the cost of raw materials at the mill will be discussed.

Quarrying.—In the following pages the term "quarrying" will be used to cover all methods of obtaining raw materials from open excavations,—quarries, cuts or pits—whether the material excavated be a limestone, a shale or a clay. Quarrying is the most natural and common method of excavating the

raw materials for cement manufacture. If marl, which is usually worked by dredging, be excluded from consideration, it is probably within safe limits to say that 95 per cent. of the raw materials used at American Portland cement plants are obtained by quarrying. If marls be included, the percentages excavated by different methods would probably be about as follows: Quarrying, 88 per cent.; dredging, 10 per cent.; mining, 2 per cent.

In the majority of limestone quarries the material is blasted out and loaded by hand on to cars or carts. In a few limestone quarries a steam shovel is employed to do the loading, and in shale quarries this use of steam shovels is more frequent. In certain clay and shale pits, where the materials are of suitable character, the steam shovel does all the work, both excavating and loading the raw materials.

The rock is usually shipped to the mill as quarried without any treatment except sledging it to convenient size for loading. At a few quarries, however, a crushing plant is installed at the quarry, and the rock is sent as crushed stone to the mill. A few plants also have installed their driers at the quarry, and dry the stone before shipping it to the mill. Except the saving of mill space thus attained, this practice seems to have little to commend it.

Mining.—The term "mining" will be used, in distinction from "quarrying," to cover methods of obtaining any kind of raw material by underground workings, through shafts or tunnels. Mining is, of course, rarely employed in excavating materials of such low value per ton as the raw materials for Portland cement manufacture. Occasionally, however, when a thin bed of limestone or shale is being worked, its dip will carry it under such a thickness of other strata as to make mining cheaper than stripping and quarrying, for that particular case.

Mining is considerably more expensive work than quarrying, but there are a few advantages about it that serve to counterbalance the greater cost per ton of raw material. A mine can be worked steadily and economically in all kinds of weather, while an open cut or quarry is commonly in a more or less unworkable condition for about three months of the year. Material won by mining is, moreover, always dry and clean.

Dredging.—The term "dredging" will be here used to cover all methods of excavating soft, wet, raw materials. The fact

that the materials are wet implies that the deposit occurs in a basin or depression; and this in turn implies that the mill is probably located at a higher elevation than the deposit of raw material, thus necessitating up-hill transportation to the mill.

The only raw material for Portland cement manufacture that is extensively worked by dredging, in the United States, is marl. Occasionally the clay used is obtained from deposits overlain by more or less water; but this is rarely done except where the marl and clay are interbedded or associated in the same deposit.

A marl deposit, in addition to containing much water diffused throughout its mass, is usually covered by a more or less considerable depth of water. This will frequently require the partial draining of the basin in order to get tracks laid near enough to be of service.

In dredging marl the excavator is frequently mounted on a barge, which floats in a channel resulting from previous investigation. Occasionally, in deposits which either were originally covered by very little water or have been drained, the shovel is mounted on a car, running on tracks laid along the edge of the deposit.

The material brought up by the dredge may be transported to the mill in two different ways, the choice depending largely upon the manufacturing processes in use at the plant. At plants using dome or chamber kilns, or where the marl is to be dried before sending to the kiln, the excavated marl is usually loaded by the shovel on cars, and hauled to the mill by horse or steam power. At normal marl plants, using a very wet mixture, it is probable that the second method of transportation is more economical. This consists of dumping the marl from the excavator into tanks, adding sufficient water to make it flow readily, and pumping the fluid mixture to the mill in pipes.

Cost of raw materials at mill.—The most natural way, perhaps, to express the cost of the raw material delivered at the mill would be to state it as being so many cents uper ton or cubic yard of raw material; and this is the method followed by quarrymen or miners in general. To the cement manufacturer, however, such an estimate is not so suitable as one based on the cost of raw materials per ton or barrel of finished cement.

In the case of hard and comparatively dry limestones or shales, it may be considered that the raw material loses 33 1-3 per cent.

in weight on burning. Converting this relation into pounds of raw material and of clinker we find that 600 pounds of dry raw material will make about 400 pounds of clinker. Allowing something for other losses in the process of manufacture, it is convenient and sufficiently accurate to estimate that 600 pounds of dry raw material will give one barrel of finished cement. These estimates must be increased if the raw material carry any appreciable amount of water. Clays will frequently contain 15 per cent. or more of water; while soft chalky limestones, if quarried during wet weather, may carry as high as 15 to over 20 per cent. A Portland cement mixture composed of a pure chalky limestone and a clay might, therefore, average 10 to 20 per cent. of water; and consequently about 700 pounds of such a mixture would be required to make one barrel of finished cement.

With marls the loss on drying and burning is much greater. Russell states* that according to determinations made by E. D. natural deposits, contains about 47 1-2 pounds of lime carbonate and 48 pounds of water. In making cement from a mixture of marl and clay, therefore, it would be necessary to figure on excavating and transporting over 1,000 pounds of raw material for every barrel of finished cement.

From the preceding notes it will be understood that the cost of raw materials at the mill, per barrel of cement, will vary not only with the cost of excavation, but with the kind of materials in use.

In dealing with hard dry materials, extracted from open quarries near the mills, the cost of raw materials may vary between 8 cents and 15 cents per barrel of cement. The lower figure named is probably about the lowest attainable with good management and under favorable natural conditions; the higher figure is probably a maximum for fairly careful management of a quarry under eastern labor conditions. When it is necessary to mine the materials, the cost will be somewhat increased. Cement rock has been mined at a cost equivalent to 10 cents per barrel of cement; but the figure is attained under particularly favorable conditions. The cost of mining and transportation may reach from this figure up to 20 cents per barrel.

*22nd Ann. Rept., U. S. Geol. Surv., pt. 3, p. 657.

METHODS OF MANUFACTURE.

If, as in the present volume, we exclude from consideration the so-called "natural Portlands," Portland cement may be regarded as being an artificial product, obtained by burning to semi-fusion an intimate mixture of pulverized materials, this mixture containing lime, silica and alumina, varying in proportion only with certain narrow limits; and by crushing finely the clinker resulting from this burning.

If this restricted definition of Portland cement be accepted, four points may be regarded as being of cardinal importance in its manufacture. These are:

(1) The cement mixture must be of the proper chemical composition.

(2) The materials of which it is composed must be carefully ground and intimately mixed before burning.

(3) The mixture must be burned at the proper temperature.

(4) After burning, the resulting clinker must be finely ground.

The first named of these points—the chemical composition of the mixture—can be more advantageously discussed after the other three points have been disposed of. The subjects will, therefore, be taken up in the following order:

Preparation of the mixture for the kiln.
Burning the mixture.
Grinding the clinker, addition of gypsum, etc.
Composition and properties of Portland cement.

PREPARATION OF THE MIXTURE FOR THE KILN.

The preparation of the mixture for the kiln involves the reduction of both of the raw materials to a very fine powder, and their intimate mixture. In practice the raw materials are usually crushed more or less finely, and then mixed, after which the final reduction to powder takes place. Two general methods of treatment—the dry and the wet—are in use at different plants. Unless the limey constituent of the mixture is a marl, already full of water, the dry method is almost invariably followed. This consists merely in keeping the materials in as dry

a condition as possible throughout the entire process of crushing and mixing; and, if the raw materials originally contained a little moisture, they are dried before being powdered and mixed. In the wet method, on the other hand, the materials are powdered and mixed while in a very fluid state, containing 60 per cent. or more of water.

Drying the Raw Materials.—With the exception of the marls and clays used in the wet method of manufacture, Portland cement materials are usually dried before the grinding is commenced. This is necessary because the raw materials, as they come from the quarry, pit or mine, will almost invariably carry appreciable, though often very small, percentages of water, which greatly reduces the efficiency of most modern types of grinding mills, and tends to clog the discharge screens.

Percentage of Water in Raw Materials.—The percentage of water thus carried by the crude raw material will depend largely on the character of the material; partly on the method of handling and storing it; and partly on weather conditions.

In the case of hard limestones, freshly quarried, the water will commonly range from 1-2 per cent. to 3 per cent., rarely reaching or exceeding the higher figure except in the very wet quarries or during a rainy season. Such limestones, comparatively dry when quarried, are frequently sent to the grinding mills without artificial drying.

With the soft, chalky limestones, which absorb water very rapidly, the percentage can usually be kept down to 5 per cent. or less in dry weather; while prolonged wet weather may necessitate the handling at the mill of material carrying as high as 15 to 20 per cent. of water.

The clays present a much more complicated case. In addition to the hydroscopic or mechanically-held water that they may contain, there is also always present a certain percentage of chemically combined water. The amount of hydroscopic water present will depnd on the treatment and exposure of the clay; and may vary from 1 per cent. or so in clays which have been stored and air-dried to as high as 30 per cent. in fresh clays. The chemically combined water will depend largely on the composition of the clay, and may vary from 5 to 12 per cent. The hygroscopic or mechanically held water of clays can be driven off at a temperature of 212° F., while the chemically

combined water is lost only at a low red heat. The total water, therefore, to be driven off from clays may range from 6 to 42 per cent., depending on the weather, the drainage of the clay pit, and the care taken in preventing unnecessary exposure to moisture of the excavated clay. The average total amount of moisture will probably be about 15 per cent.

In dealing with shales, the mechanically-held water will rarely rise above 10 per cent., and can commonly be kept well below that limit. An additional 2 to 7 per cent. of water will be carried, by any shale, in a state of chemical combination.

At a few plants marl is used, with clay, in a dry process. As noted elsewhere, the marls, as excavated, carry usually about 50 per cent. of water. This case presents a more difficult problem than do the other raw materials, because the vegetable matter usually present in marls is extremely retentive of water.

It will be seen, therefore, that cement materials may carry from 1 per cent. to 50 per cent. of water when they reach the mill. In a dry process it is necessary to remove practically all of this water before commencing the grinding of the materials. One reason for this is that fine pulverizing can not be economically or satisfactorily accomplished unless absolutely dry material is fed to the grinding machinery.

Another reason, which is one of convenience rather than of necessity, is that the presence of water in the raw materials complicates the calculation of the cement mixture.

Methods and cost of drying.—The type of dryer commonly used in cement plants is a cylinder approximately 5 feet in diameter and 40 feet or so in length, set at a slight inclination to the horizontal, and rotating on bearings. The wet raw material is fed in at the upper end of the cylinder, and it moves gradually toward the lower end, under the influence of gravity, as the cylinder revolves. In many dryers angle irons are bolted to the interior in such a way as to lift and drop the raw material alternately, thus exposing it more completely to the action of the heated gases, and materially assisting in the drying process. The dried raw material falls from the lower end of the cylinder into an elevator boot, and is then carried to the grinding mills.

The drying cylinder is heated either by a separate furnace or by waste gases from the cement kiln. In either case the pro-

ducts of combustion are introduced into the cylinder at its lower end, and drawn through it, and escape up a stack set at the upper end of the dryer.

The dryer above described is the simplest, and is most commonly used. For handling the small percentages of water contained in most cement materials it is very efficient, but for dealing with high percentages of water, such as are encountered when marl is to be used in a dry process, it seems probable that double-heating dryers will be found more economical. This type is exemplified by the Ruggles-Coles dryer, in which a double cylinder is employed. The wet raw material is fed into the space between the inner and outer cylinders, while the heated gases pass first through the inner cylinder, and then, in a reverse direction, through the space between the inner and outer cylinders. This double-heating type of dryer is employed in almost all of the slag cement plants in the United States, and is also in use in several Portland cement plants.

When vertical kilns were in use, drying floors and drying tunnels were extensively used, but at present they can be found in only a few places, being everywhere else supplanted by the rotary dryers.

The cost of drying will depend on the cost of fuel, the percentage of water in the wet material and the type of dryer. Even under the most unfavorable conditions five pounds of water can be expected to be evaporated per pound of coal used, while a good dryer will usually evaporate seven or eight pounds of water per pound of coal.

GRINDING AND MIXING—DRY METHODS.—Part at least of the grinding is usually accomplished before the drying, but for convenience the subjects have been separated in the present paper. Usually the limestone is sent through a crusher at the quarry or mill before being dried, and occasionally the raw material is further reduced in a Williams mill, etc., before drying, but the principal part of the reduction always takes place after the material has been dried.

After the two raw materials have been separately dried they may be mixed immediately, or each may be further reduced separately before mixing. Automatic mixers, of which many types are on the market, give a mixture in proportions determined upon from analysis of the materials.

The further reduction of the mixture is usually carried on in two stages, the material being ground to say 30 mesh in a ball mill, komminuter, Griffin mill, etc., and finally reduced in a tube mill. At a few plants, however, single stage reduction is practiced in Griffn or Huntington mills, while at the Edison plant at Stewartsville, N. J., the reduction is accomplished in a series of rolls.

The majority of plants use either the Griffin mill and tube mill or the ball and tube mills, and there is probably little difference in the cost of operating these two combinations. The ball mill has never been quite as much of a success as its companion, the tube mill, and has been replaced at several plants by the komminuter.

Fineness of Mixture.—After its final reduction, and when ready for burning, the mixture will usually run from 90 to 95 per cent. through a 100-mesh sieve. In the plants of the Lehigh district the mixture is rarely crushed as fine as when limestone and clay are used. Newberry* has pointed out in explanation for this that an argillaceous limestone (cement rock) mixed with a comparatively small quantity of purer limestone, as in the Lehigh plants, requires less thorough mixing and less fine grinding than when a mixture of limestone and clay (or marl and clay) is uesd, for even the coarser particles of the argillaceous limestone will vary so little in chemical composition from the proper mixture as to affect the quality of the resulting cement but little, should either mixing or grinding be incompletely accomplished.

A very good example of typical Lehigh Valley grinding of raw material is afforded by a specimen examined* by Prof. E. D. Campbell. This specimen of raw mix ready for burning was furnished by one of the best of the eastern Pennsylvania cement plants. A mechanical analysis of it showed the following results:

	Mesh of sieve.		
	50	100	200
Per cent. passing	96.9%	85.6%	72.4%
Per cent. residue	3.1%	14.4%	27.6%

The material, therefore, is so coarsely ground that only a trifle over 85 per cent. passes a 100-mesh sieve.

*Twentieth Ann. Rept. U. S. Geol. Surv., Pt. 6, p. 545.
*Journal Amer. Chem. Soc., vol. 25.

GRINDING AND MIXING—SLAG-LIMESTONE MIXTURES.—While the manufacture of Portland cement from a mixture of slag and limestone is similar in general theory and practice to its manufacture from a limestone-clay mixture, certain interesting difference occur in the preparation of the mixture. In the following paragraphs the general methods of preparing mixtures of slag and limestone for use in Portland cement manufacture will first be noted, after which certain processes peculiar to the use of this particular mixture will be described separately.

General methods.—After it had been determined that the pozzuolanic cement made* by mixing slag with lime without subsequent burning of the mixture, was not an entirely satisfactory structural material, attention was soon directed toward the problem of making a true Portland cement from such slag. The blast-furnace slags commonly available, while carrying enough silica and alumina for a cement mixture, are too low in lime to be suitable for Portland cement. Additional lime must be added, usually in the form of limestone; the slag and limestone must be well mixed and the mixture properly burned. The general methods for accomplishing the proper mixture of the materials vary in details. It seems probable that the first method used in attempting to make a true Portland cement from slag, was to dump the proper proportion of limestone, broken into small lumps, into molten slag. The idea was that both mixing and calcination could thus be accomplished in one stage; but in practice it was found that the resulting cement was variable in composition and always low in grade. This method has accordingly fallen into disuse, and at present three different general processes of preparing the mixture are practiced at different European and American plants.

1. The slag is granulated, dried, and ground, while the limestone is dried and ground separately. The two materials are then mixed in proper proportions, the mixture is finely pulverized in tube mills, and the product is fed in a powdered state to rotary kilns.

2. The slag is granulated, dried, and mixed with slightly less than the calculated proper amount of limestone, which has been previously dried and powdered. To this mixture is added

*See Municipal Engineering, vol. 24, p. 335, May, 1903.

sufficient powdered slaked lime (say 2 to 6 per cent.) to bring the mixture up to correct composition. The intimate mixture and final reduction are then accomplished in ball and tube mills. About 8 per cent. of water is then added, and the slurry is made into bricks, which are dried and burned in a dome or chamber kiln.

3. Slag is granulated and mixed, while still wet, with crushed limestone in proper proportions. This mixture is run through a rotary calciner, heated by waste kiln gases, in which the temperature is sufficient not only to dry the mixture, but also to partly powder it, and to reduce most of the limestone to quicklime. The mixture is then pulverized and fed into rotary kilns.

Of the three general processes above described, the second is unsuited to American conditions. The first and third are adapted to the use of the rotary kiln. The third seems to be the most economical, and has given remarkably low fuel consumption in practice, but so far has not been taken up in the United States.

Certain points of manufacture peculiar to the use of mixtures of slag and limestone will now be described.

Composition of the slag.—The slags available for use in Portland cement manufacture are of quite common occurrence in iron-producing districts. Those best suited for such use are the more basic blast-furnace slags, and the higher such slags run in lime the more available they are for this use. The slags utilized will generally run from 30 to 40 per cent. lime. The presence of over 3 per cent. or so of magnesia in a slag is of course enough to render its use as a Portland cement material inadvisable; and on this account slags from furnaces using dolomite (magnesian limestone) as a flux, are unsuited for cement manufacture. The presence of any notable percentage of sulphur is also a drawback, though, as will be later noted, part of the sulphur in the slag will be removed during the process of manufacture.

Granulation of slag.—If slag be allowed to cool slowly it solidifies into a dense, tough material, which is not readily reduced to the requisite fineness for a cement mixture. If it be cooled suddenly, however, as by bringing the stream of molten slag into contact with cold water, the slag is "granulated," *i. e.*, it breaks up into small porous particles. This granulated slag or "slag sand" is much more readily pulverized than a slowly

cooled slag; its sudden cooling has also intensified the chemical activity of its constituents so as to give it hydraulic properties, while part of the sulphur contained in the original slag has been removed. The sole disadvantage of the process of granulating slag is that the product contains 20 to 40 per cent. of water, which must be driven off before the granulated slag is sent to the grinding machinery.

In practice the granulation of the slag is effected by directing the stream of molten slag direct from the furnace into a sheet-iron through. A small stream of water flows along this trough, the quantity and rate of flow of the water being regulated so as to give complete granulation of the slag without using an excessive amount of water. The trough may be so directed as to discharge the granulated slag into tanks or into box cars, which are usually perforated at intervals along the sides so as to allow part of the water to drain off.

Drying the slag.—As above noted, the granulated slag may carry from 20 to 40 per cent. of water. This is removed by treating the slag in rotary dryers. In practice such driers give an evaporation of 8 to 10 pounds of water per pound of coal. The practice of slag drying is very fully described in Vol. 10 of the Mineral Industry, pages 84-95, where figures and descriptions of various driers are also given, with data on their evaporative efficiency. As noted earlier in this article, one of the methods of manufacturing Portland cement from slag puts off the drying of the slag until after it has been mixed with the limestone, and then accomplishes the drying by utilizing waste heat from the kilns. Kiln gases could of course be used anyway in the slag driers, but it so happens that they have not been so used except in plants following the method in question.

Grinding the slag.—Slag can be crushed with considerable ease to about 50 mesh, but notwithstanding its apparent brittleness it is difficult to grind it finer. Until the introduction of the tube mill in fact it was almost impossible to reduce this material to the fineness necessary for a cement mixture, and the proper grinding of the slag is still an expensive part of the process, as compared with the grinding of limestone, shales, or clay.

Composition of the limestone.—As the slag carries all the silica and alumina necessary for the cement mixture, the limestone to be added to it should be simply a pure lime carbonate.

The limestone used for flux at the furnace which supplies the slag will usually be found to be of suitable composition for use in making up the cement mixture.

Economics of using slag-limestone mixtures.—The manufacture of a true Portland cement from a mixture of slag and limestone presents certain undoubted advantages over the use of any other raw materials, while it has also a few disadvantages.

Probably the most prominent of the advantages lies in the fact that the most important raw material—the slag—can usually be obtained more cheaply than an equal amount of natural raw material could be quarried or mined. The slag is a waste product, and a troublesome material to dispose of, for which reasons it is obtained at small expense to the cement plant. Another advantage is due to the occurrence of the lime in the slag as oxide, and not as carbonate. The heat necessary to drive off the carbon dioxide from an equivalent mass of limestone is therefore saved when slag forms part of the cement mixture, and very low fuel consumption is obtained when slag-limestone mixture is burned.

Of the disadvantages, the toughness of the slag and the necessity for drying it before grinding are probably the most important. These serve to partly counterbalance the advantages noted above. A third difficulty, which is not always apparent at first, is that of securing a proper supply of suitable slag. Unless the cement plant is closely connected in ownership with the furnaces from which its slag supply is to be obtained, this difficulty may become very serious. In a season when a good iron market exists the furnace manager will naturally give little thought to the question of supplying slag to an independent cement plant.

The advantages of the mixture, however, seem to outweigh its disadvantages, for the manufacture of Portland cement from slag is now a large and growing industry in both Europe and America. Two Portland cement plants using slag and limestone as raw materials have been established for some time in this country, several others are in course of construction at present, and it seems probable that in the near future Alabama will join Illinois and Pennsylvania as an important producer of Portland cement from slag.

Grinding and Mixing—Wet Methods.—Wet methods of preparing Portland cement mixtures date back to the time when millstones and similar crude grinding contrivances were in use. With such imperfect machinery it was almost impossible to grind dry materials fine enough to give a good Portland cement mixture. The advent of good grinding machinery has practically driven out wet methods of manufacture in this country, except in dealing with materials such as marls, which naturally carry a large percentage of water. One or two plants in the United States do, it is true, deliberately add water to a limestone-clay mixture; but the effect of this practice on the cost sheets of these remarkable plants is not encouraging.

In preparing cement mixtures from marl and clay, a few plants dry both materials before mixing. It seems probable that this practice will spread, for the wet method of mixture is inherently expensive. At present, however, almost all marl plants use wet methods of mixing, and it is therefore necessary to give some space to a discussion of such methods.

Certain points regarding the location, physical condition, and chemical composition of the marls and clays used in such mixtures have important effects upon the cost of the wet process. As regards location, considered on a large scale, it must be borne in mind that marl deposits of workable size occur only in the Northern States and in Canada. In consequence the climate is unfavorable to continuous working throughout the year, for the marl is usually covered with water, and in winter it is difficult to secure the material. In a minor sense location is still an important factor, for marl deposits necessarily and invariably are found in depressions; and the mill must, therefore, just as necessarily, be located at a higher level than its source of raw material, which involves increased expense in transporting the raw material to the mill.

Glacial clays, which are usually employed in connection with marl, commonly carry a much larger proportion of sand and pebbles than do the sedimentary clays of more southern regions.

The effect of the water carried by the marl has been noted on an earlier page. The material as excavated will consist approximately of equal weights of lime carbonate and of water. This on the face of it would seem to be bad enough as a business proposition; but we find that in practice more water is often added to permit the marl to be pumped up to the mill.

On the arrival of the raw materials at the mill the clay is often dried, in order to simplify the calculation of the mixture. The reduction of the clay is commonly accomplished in a disintegrator or in edge-runner mills, after which the material is further reduced in a pug mill, sufficient water being here added to enable it to be pumped readily. It is then ready for mixture with the marl, which at some point in its course has been screened to remove stones, wood, etc., so far as possible. The slurry is further ground in pug mills or wet grinding mills of the disk type; while the final reduction takes place commonly in wet tube mills. The slurry, now containing 30 to 40 per cent. of solid matter and 70 to 60 per cent. of water, is pumped into storage tanks, where it is kept in constant agitation to avoid settling. Analyses of the slurry are taken at this point, and the mixture in the tanks is corrected if found to be of unsatisfactory composition. After standardizing, the slurry is pumped into the rotary kilns. Owing to the large percentage of water contained in the slurry the fuel consumption per barrel of finished cement is 30 to 50 per cent. greater, and the output of each kiln correspondingly less than in the case of a dry mixture.

It may be of interest, for comparison with the above description of the wet process with rotary kilns, to insert a description of the semi-wet process as carried on a few years ago at the dome kiln plant of the Empire Portland Cement Company at Warners, N. Y. The plant has been remodeled since that date, but the processes formerly followed are still of interest, as they resulted in a high-grade though expensive product.

At the Empire plant the marl and clay were obtained from a swamp about three-fourths of a mile from the mill. A revolving derrick with clam-shell bucket was employed for excavating the marl, while the clay was dug with shovels. The materials were taken to the works over a private narrow-gauge road, on cars, carrying about three tons each, drawn by a small locomotive. At the mill the cars were hauled up an inclined track, by means of a cable and drum, to the mixing floor.

The clay was dried in three Cummer "Salamander" driers, after which it was allowed to cool, and then carried to the mills. These mills were of the Sturtevant "rock emery" type, and reduced the clay to a fine powder, in which condition it was fed, after being weighed, to the mixer. The marl was weighed and sent directly to the mixer, no preliminary treatment being neces-

sary. The average charge was about 25 per cent. clay and about 75 per cent. marl.

The mixing was carried on in a mixing pan 12 feet in diameter, in which two large rolls, each about 5 feet in diameter, and 16-inch face, ground and mixed the materials thoroughly. The mixture was then sampled and analyzed, after which it was carried by a belt conveyor to two pug mills, where the mixing was completed and the slurry formed into slabs about 3 feet long and 4 to 5 inches in width and height. These on issuing from the pug mill were cut into a number of sections, so as to give bricks about 6 inches by 4 inches by 4 inches in size. The bricks were then placed on slats, which were loaded on rack cars and run into the drying tunnels. The tunnels were heated by waste gases from the kilns and required from twenty-four to thirty-six hours to dry the bricks.

After drying the bricks were fed into dome kilns, twenty of which were in use, being charged with alternate layers of coke and slurry bricks. The coke charge for a kiln was about four or five tons, and this produced 20 to 26 tons of clinker at each burning, thus giving a fuel consumption of about 20 per cent. as compared with the 40 per cent. or so required in the rotary kilns using wet materials. From thirty-six to forty hours were required for burning the charge. After cooling, the clinker was shoveled out, picked over by hand, and reduced in a Blake crusher, Smidth ball mills, and Davidsen tube mills.

Composition of mixture.—The cement mixture ready for burning will commonly contain from 74 to 77.5 per cent. of lime carbonate, or an equivalent proportion of lime oxide. Several analyses of actual cement mixtures are given in the following table. Analysis No. 1, with its relatively high percentage of magnesia, is fairly typical of Lehigh Valley practice. Analyses Nos. 2 and 3 show mixtures low in lime, while analysis No. 4 is probably the best proportioned of the four, especially in regard to the ratio between silica and alumina plus iron. This ratio, for ordinary purposes, should be about 3.-, as the cement becomes quicker setting and lower in ultimate strength as the percentage of alumina increases. If the alumina percentage be carried too high, moreover, the mixture will give a fusible, sticky clinker when burned, causing trouble in the kilns.

Analyses of cement mixtures.

	1	2	3	4
Silica	12.62	13.46	13.85	11.77
Alumina and iron oxide	6.00	?	7.20	4.35
Carbonate of lime	75.46	73.66	73.93	76.84
Magnesia	2.65	?	?	1.74

BURNING THE MIXTURE.

After the cement mixture has been carefully prepared, as described in preceding pages, it must be burned with equal care.

In the early days of the Portland cement industry a simple vertical kiln, much like that used for burning lime and natural cement, was used for burning the Portland cement mixture. These kilns, while fairly efficient so far as fuel consumption was concerned, were expensive in labor, and their daily output was small. In France and Germany they were soon supplanted by improved types, but still stationary and vertical, which gave very much lower fuel consumption. In America, however, where labor is expensive while fuel is comparatively cheap, an entirely different style of kiln has been evolved. This is the rotary kiln. With the exception of a very few of the older plants, which have retained vertical kilns, all American Portland cement plants are now equipped with rotary kilns.

The history of the gradual evolution of the rotary kiln is of great interest, but as the subject can not be taken up here, reference should be made to the papers cited below* in which details, accompanied often by illustrations of early types of rotary kilns are given.

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*Duryee, E., The first manufacture of Portland cement by the direct rotary kiln process. Engineering News, July 26, 1900.

Lesley, R. W., History of the Portland cement industry in the United States. 8 vo. pp. 146, Philadelphia, 1900.

Lewis, F. H., The American rotary kiln process for Portland cement, in The Cement Industry, pp. 188-199, New York, 1900.

Matthey, H., The invention of the new cement burning method. Engineering and Mining Journal, vol. 67, pp. 555, 705; 1899.

Stanger, W. H., and Blount, B., The rotary process of cement manufacture. Proc. Institution Civil Engineers, vol. 145, pp. 44-136; 1901.

Editorial, The influence of the rotary kiln on the development of Portland cement manufacture in America. Engineering News, May 3, 1900.

The design, construction and operation of the vertical stationary kilns of various types is discussed in many reports in Portland cement, the most satisfactory single paper being probably that referred to below*. As the subject is, in America at least, a matter of simply historical interest, no description of these kilns or their operation will be given in the present bulletin.

At present, practice in burning at the different American cement plants is rapidly approaching uniformity, though differences in materials, etc., will always prevent absolute uniformity from being reached. The kiln in which the material is burned is now almost invariably of the rotary type, the rotary process, which is essentially American in its development, being based upon the substitution of machines for hand labor wherever possible. A brief summary of the process will first be given, after which certain subjects of interest will be taken up in more detail.

Summary of burning process.—As at present used, the rotary kiln is a steel cylinder about 6 feet in diameter; its length, for dry materials, is usually 60 or 80 feet, while for wet mixtures an 80-foot, or even longer, kiln is frequently employed.

This cylinder is set in a slightly inclined position, the inclination being approximately one-half inch to the foot. The kiln is lined, except near the upper end, with very resistant fire brick, to withstand both the high temperature to which its inner surface is subjected and also the destructive action of the molten clinker.

The cement mixture is fed in at the upper end of the kiln, while fuel (which may be either powdered coal, oil, or gas), is injected at its lower end. The kiln, which rests upon geared bearings, is slowly revolved about its axis. This revolution, in connection with the inclination at which the cylinder is set, gradually carries the cement mixture to the lower end of the kiln. In the course of this journey the intense heat generated by the burning fuel first drives off the water and carbon dioxide from the mixture, and then causes the lime, silica, alumina, and

*Stanger, W. H., and Blount, B., Gilbert, W., and Candlot, E., (Discussion of the value, design and results obtained from various types of fixed kilns). Proc. Institution Civil Engineers, vol. 145, pp. 44, 48, 81, 82, 99, 100; 1901.

iron to combine chemically to form the partially fused mass known as "cement clinker." This clinker drops out of the lower end of the kiln, is cooled so as to prevent injury to the grinding machinery, and is then sent to the grinding mills.

Theoretical fuel requirements.—As a preliminary to a discussion of actual practice in the matter of fuel, it will be of interest to determine the heat units and fuel theoretically required in the manufacture of Portland cement from a dry mixture of normal composition.

In burning such a mixture to a clinker, practically all of the heat consumed in the operation will be that required for the dissociation of the lime carbonate present into lime oxide and carbon dioxide. Driving off the water of combination that is chemically held by the clay or shale, and decomposing any calcium sulphate (gypsum) that may be present in the raw materials, will require a small additional amount of heat. The amount required for these purposes is not accurately known, however, but is probably so small that it will be more or less entirely offset by the heat which will be liberated during the combination of the lime with the silica and alumina. We may, therefore, without sensible error, regard the total heat theoretically required for the production of a barrel of Portland cement as being that which is necessary for the dissociation of 450 pounds of lime carbonate. With coal of a thermal value of 13,500 B. T. U., burned with only the air supply demanded by theory, this dissociation will require 25½ pounds of coal per barrel of cement, a fuel consumption of only 6.6 per cent.

Losses of heat in practice.—In practice with the rotary kiln, however, there are a number of distinct sources of loss of heat, which result in a fuel consumption immensely greater than the theoretical requirements given above. The more important of these sources of loss are the following:

1. The kiln gases are discharged at a temperature much above that of the atmosphere, ranging from 300°F. to 2,000°F., according to the type of materials used and the length of the kiln.

2. The clinker is discharged at a temperature varying from 300°F. to 2,500°F., the range depending, as before, on materials and length of the kiln.

3. The air supply injected into the kiln is always greater, and usually very much greater, than that required for the perfect combusion of the fuel; and the available heating power of the fuel is thereby reduced.

4. Heat is lost by radiation from the ends and exposed surfaces of the kiln.

5. The mixture, in plants using a wet process, carries a high percentage of water, which must be driven off.

It is evident, therefore, that present-day working conditions serve to increase greatly the amount of fuel actually necessary for the production of a barrel of cement above that required by theory.

Actual fuel requirements and output.—Rotary kilns are nominally rated at a production of 200 barrels per day per kiln. Even on dry and easily clinkered materials and with good coal, however, such an output is not commonly attained with a 60-foot kiln, except in the Lehigh district. Normally a kiln working on a dry mixture will produce from 160 to 180 barrels of cement per day of twenty-four hours. In doing this, if good coal is used, its fuel consumption will commonly be from 120 to 140 pounds of coal per barrel of cement, though it may range as high as 160 pounds, and, on the other hand, has fallen as low as 90 pounds. An output of 175 barrels per day, with a coal consumption of 130 pounds per barrel, may therefore be considered as representing the results of fairly good practice on dry materials with a 60-foot kiln. In dealing with a wet mixture, which may carry anywhere from 30 to 70 per cent. of water, the results are more variable, though always worse than with dry materials. In working a 60-foot kiln on wet material, the output may range from 80 to 120 barrels per day, with a fuel consumption of from 150 to 230 pounds per barrel. Using a longer kiln, partly drying the mixture, and utilizing waste heat, will of course improve these figures materially.

When the heavy Western oils are used for kiln fuel, it may be considered that one gallon of oil is equivalent in the kiln to about ten pounds of coal. The fuel consumption, using dry materials, will range between 11 and 14 gallons of oil per barrel of cement; but the output per day is always somewhat less with oil fuel than where coal is used.

Natural gas in the kiln may be compared with good Pennsylvania coal by allowing about 20,000 to 30,000 cubic feet of gas

as equivalent to a ton of coal. This estimate is, however, based upon too little data to be as close as those above given for oil or coal.

Effect of composition on burning.—The differences in composition between Portland cement mixtures are very slight if compared, for example, to the differences between various natural cement rocks. But even such slight differences as do exist exercise a very appreciable effect on the burning of the mixture. Other things being equal, any increase in the percentage of lime in the mixture will necessitate a higher temperature in order to get an equally sound cement. A mixture which will give a cement carrying 59 per cent. of lime, for example, will require much less thorough burning than would a mixture designed to give a cement with 64 per cent. of lime.

With equal lime percentages, the cement carrying high silica and low alumina and iron will require a higher temperature than if it were lower in silica and higher in alumina and iron. But, on the other hand, if the alumina and iron are carried too high, the clinker will ball up in the kiln, forming sticky and unmanageable masses.

Character of kiln coal.—The fuel most commonly used in modern rotary kiln practice is bituminous coal, pulverized very finely. Coal for this purpose should be high in volatile matter, and as low in ash and sulphur as possible. Russell gives the following analyses of West Virginia and Pennsylvania coals used at present at various cement plants in Michigan.

Analyses of kiln coals.

	1	2	3	4
Fixed carbon	56.15	56.33	55.82	51.69
Volatile matter	35.41	35.26	39.37	39.52
Ash	6.36	7.06	3.81	6.13
Moisture	2.08	1.35	1.00	1.40
Sulphur	1.30	1.34	0.42	1.46

The coal as usually bought is either "slack" or "run of mine." In the latter case it is necessary to crush the lumps before proceeding further with the preparation of the coal, but with slack this preliminary crushing is not necessary, and the material can go directly to the dryer.

Drying coal.—Coal as bought may carry as high as 15 per cent. of water in winter or wet season. Usually it will run from 3 to 8 per cent. To secure good results from the crushing machinery it is necessary that this water should be driven off. For coal drying, as for the drying of raw materials, the rotary dryer seems best adapted to American conditions. It should be said, however, that in drying coal it is usually considered inadvisable to allow the products of combustion to pass through the cylinder in which the coal is being dried. This restriction serves to decrease slightly the possible economy of the dryer, but an evaporation of 6 to 8 pounds of water per pound of fuel coal can still be counted on with any good dryer. The fuel cost of drying coal containing 8 per cent. of moisture, allowing $2 per ton for the coal used as fuel, will therefore be about 3 to 4 cents per ton of dried product.

Pulverizing coal.—Though apparently brittle enough when in large lumps, coal is a difficult material to pulverize finely. For cement kiln use, the fineness of reduction is very variable. The finer the coal is pulverized the better results will be obtained from it in the kiln; and the poorer the quality of the coal the finer it is necessary to pulverize it. The fineness attained may therefore vary from 85 per cent. through a 100-mesh sieve, to 95 per cent. or more, through the same. At one plant a very poor but cheap coal is pulverized to pass 98 per cent. through a 100-mesh sieve, and in consequence gives very good results in the kiln.

Coal pulverizing is usually carried on in two stages, the material being first crushed to 20 to 30 mesh in a Williams mill or ball mill, and finally reduced in a tube mill. At many plants, however, the entire reduction takes place in one stage, Griffin or Huntington mills being used.

Total cost of coal production.—The total cost of crushing (if necessary), drying and pulverizing coal, and of conveying and feeding the product to the kiln, together with fair allowance for replacements and repairs, and for interest on the plant, will probably range from about 20 to 30 cents per ton of dried coal, for a 4-kiln plant. This will be equivalent to a cost of from 3 to 5 cents per barrel of cement. While this may seem a heavy addition to the cost of cement manufacture, it should be remembered that careful drying and fine pulverizing enable the manu-

facturer to use much poorer—and therefore cheaper—grades of coal than could otherwise be utilized.

CLINKER GRINDING. GYPSUM.

Clinker grinding.—The power and machinery required for pulverizing the clinker at a Portland cement plant using the dry process of manufacture is very closely the same as that required for pulverizing the raw materials for the same output. This may seem, at first sight, improbable, for Portland cement clinker is much harder to grind than any possible combination of raw materials; but it must be remembered that for every barrel of cement produced about 600 pounds of raw materials must be pulverized, while only a scant 400 pounds of clinker will be treated, and that the large crushers required for some raw materials can be dispensed with in crushing clinker. With this exception, the raw material side and the clinker side of a dry-process Portland cement plant are usually almost or exactly duplicates.

The difficulty, and in consequence the expense, of grinding clinker will depend in large part on the chemical composition of the clinker and on the temperature at which it has been burned. The difficulty of grinding, for example, increases with the percentage of lime carried by the clinker; and a clinker containing 64 per cent. of lime will be very noticeably more resistant to pulverizing than one carrying 62 per cent. of lime. So far as regards burning, it may be said in general, that the more thoroughly burned the clinker the more difficult it will be to grind, assuming that its chemical composition remains the same.

The tendency among engineers at present is to demand more finely ground cement. While this demand is doubtless justified by the results of comparative tests of finely and coarsely ground cements, it must be borne in mind that any increase in fineness of grinding means a decrease in the product per hour of the grinding mills employed, and a consequent increase in the cost of cement. At some point in the process, therefore, the gain in strength due to fineness of grinding will be counterbalanced by the increased cost of manufacturing the more finely ground product.

The increase in the required fineness has been gradual but steady during recent years. Most specifications now require at

least 90 per cent. to pass a 100-mesh sieve; a number require 92 per cent.; while a few important specifications require 95 per cent. Within a few years it is probable that almost all specifications will go as high as this.

Addition of gypsum.—The cement produced by the rotary kiln is invariably naturally so quick-setting as to require the addition of sulphate of lime. This substance, when added in quantities up to 2½ or 3 per cent., retards the rate of set of the cement proportionately, and appears to exert no injurious influence on the strength of the cement. In amount over 3 per cent., however, its retarding influence seems to become at least doubtful, while a decided weakening of the cement is noticeable.

Sulphate of lime may be added in one of two forms: either as crude gypsum or as burned plaster. Crude gypsum is a natural hydrous lime sulphate, containing about 80 per cent. of lime sulphate and 20 per cent. of water. When gypsum is calcined at temperatures not exceeding 400° F., most of its contained water is driven off. The "plaster" remaining carries about 93 per cent. of lime sulphate, with only 7 per cent of water.

In Portland cement manufacture either gypsum or burned plaster may be used to retard the set of the cement. As a matter of fact, gypsum is the form almost universally employed in the United States. This is merely a question of cost. It is true that to secure the same amount of retardation of set it will be necessary to add a little more of gypsum than if burned plaster were used; but, on the other hand, gypsum is much cheaper than burned plaster.

The addition of the gypsum to the clinker is usually made before it has passed into the ball mill, komminuter, or whatever mill is in use for preliminary grinding. Adding it at this point secures much more thorough mixing and pulverizing than if the mixture were made later in the process. At some of the few plants which use plaster instead of gypsum, the finely ground plaster is not added until the clinker has received the final grinding and is ready for storage or packing.

CONSTITUTION OF PORTLAND CEMENT.

During recent years much attention has been paid by various investigators to the constitution of Portland cement. The chemical composition of any particular sample can, of course, be

readily determined by analysis; and by comparison of a number of such analyses, general statements can be framed as to the range in composition of good Portland cements.

The chemical analyses will determine what ingredients are present, and in what percentages, but other methods of investigation are necessary to ascertain in what manner these various ingredients are combined. A summary of the more important results brought out by these investigations on the constitution of Portland cement is here given.

It would seem to be firmly established that, in a well-burned Portland cement, much of the lime is combined with most of the silica to form the compound 3 CaO, SiO_2,—tricalcic silicate. To this compound is ascribed, in large measure, the hydraulic properties of the cement; and in general it may be said that the value of a Portland cement increases directly as the proportion of 3 CaO, SiO_2. The ideal Portland cement, toward which cements as actually made tend in composition, would consist exclusively of tricalcic silicate, and would be therefore composed entirely of lime and silica in the following proportions:

Lime (CaO)	73.6
Silica (SiO_2)	26.4

Such an ideal cement, however, can not be manufactured under present commercial conditions, for the heat required to clinker such a mixture can not be attained in any working kiln. Newberry has prepared such mixtures by using the oxy-hydrogen blowpipe; and the electrical furnace will also give clinker of this composition; but a pure lime-silica Portland is not possible under present-day conditions.

In order to prepare Portland cement in actual practice, therefore, it is necessary that some other ingredient or ingredients should be present to serve as a flux in aiding the combination of the lime and silica, and such aid is afforded by the presence of alumina and iron oxide.

Alumina (Al_2O_3) and iron oxide (Fe_2O_3), when present in noticeable percentages, serve to reduce the temperature at which combination of the lime and silica (to form 3 CaO, SiO_2) takes place; and this clinkering temperature becomes further and further lowered as the percentages of alumina and iron are increased. The strength and value of the product, however, also decrease as the alumina and iron increase; so that in actual

practice it is necessary to strike a balance between the advantage of low clinkering temperature and the disadvantage of weak cement, and to thus determine how much alumina and iron should be used in the mixture.

It is generally considered that whatever alumina is present in the cement is combined with part of the lime to form the compound 2 CaA, SiO_2,—dicalcic aluminate. It is also held by some, but this fact is somewhat less firmly established than the last, that the iron present is combined with the lime to form the compound 2 CaO, Fe_2O_3. For the purposes of the present paper, it will be sufficient to say that, in the relatively small percentages in which iron occurs in Portland cement, it may for convenience be considered as almost equivalent to alumina and its action, and the two may be calculated together.

PART II.

THE CEMENT RESOURCES OF ALABAMA.

BY EUGENE A. SMITH.

In Alabama is found an extensive series of limestones capable of furnishing excellent raw material for the manufacture of Portland cement, while the shales and clays necessary to complete the mixture are found in every county in the State. As a matter of convenience, the Portland cement materials of northern Alabama and of central and southern Alabama will be discussed separately, because there is a marked geologic as well as geographic distinction between the two portions of the State.

CHAPTER 1.

THE PORTLAND CEMENT MATERIALS OF NORTHERN ALABAMA.

The raw materials for the manufacture of Portland cement occurring in the Paleozoic formations of northern Alabama are limestones, shales, and clays. Of these the limestones belong mainly to the Lower Carboniferous and the Trenton formations; the shales to the Coal Measures, and the clays to the Cambrian, Lower Carboniferous, and Coal Measures. Although as yet these materials have not been utilized for this purpose in Alabama, they have been so used in other States, and there is no reason to doubt that the future will witness their utilization in Alabama.

AVAILABLE LIMESTONES.

General geology.—In northern Alabama the combined effects of geologic structure and erosion have resulted in certain definite topographic types, with which the geologic outcrops are closely connected.

Structurally northern Alabama is made up of a series of parallel synclines and anticlines, trending usually a little north of east. The anticlines are sharp, narrow folds; the synclines are flat, wide basins. The effect of erosion has been to cut away the anticlines and the streams of the region now run along anticlinal valleys bordered by flat-topped synclinal plateaus.

The plateaus throughout most of northern Alabama are capped by conglomerates, shales, and sandstones of the Coal Measures. The lower Carboniferous limestones commonly outcrop along the sides and at the immediate base of the plateaus. The lower Silurian beds occur as long, narrow outcrops in the valleys. The middle of the valley is usually occupied by Cambrian shales and the Knox dolomite. The Trenton limestones would normally outcrop as two parallel bands in each valley—between the middle of the valley and the foothills of the plateaus. Faulting has, however, been so common that only one of these bands is usually present, the other being cut out by a fault.

Lower Carboniferous.—Limestones of suitable quality for cement manufacture occur in the Mountain limestone or Chester formation of the lower Carboniferous. Perhaps the most accessible occurrences of this rock are in the Tennessee Valley to the west of Tuscumbia and south of the river and railroad. Here the quarries of Fossick & Co. were formerly located. Their quarries at this time are farther eastward, but at a greater distance from the river, in Lawrence county north of Russellville. This outcrop extends thence eastward along the base of Little Mountain as far as Whitesburg, above which place to Guntersville the river flows through a valley floored with lower Carboniferous limestone. The Southern Railway passes over outcrops of this rock in most of the mountain coves east of Huntsville, and from Scottsboro to the Tennessee line the country rock is almost entirely of this formation. The Louisville and Nashville Railroad south of Decatur nearly to Wilhite is mostly in the same formation. These two lines, together

with the Tennessee river, would provide ample means of transportation for the rock or for the finished product. Analysis of the rock from the Fossick quarries is given in Table A.

In Browns Valley south of Brooksville the Mountain limestone is the prevailing rock across the valley, and at Bangor and Blount Springs, on the Louisville and Nashville Railroad, there are extensive quarries which have been worked for many years to supply rock for fluxing purposes to the furnaces of the Birmingham district. Analyses Nos. 2, 3, 4, 5, 6, 7, 8, and 9, Table A, show the composition of average samples from these quarries; 5 to 9, inclusive, are of carload samples.

From Brooksville to the Tennessee line a great thickness of this limestone is exposed along the western escarpment of Sand Mountain, below the sandstones of the Coal Measures, which there cap the mountain. In this area the river runs near the foot of the mountain and would afford the means of transportation.

In similar manner the lower Carboniferous limestone outcrops along the western flank of Lookout Mountain in Little Wills Valley, from near Attalla to the Georgia line, and south of Attalla it forms the lower part of the escarpments of Blount and Chandlers Mountains. The Alabama Great Southern Railroad passes very near to the outcrop from the Georgia line down to Springville, Ala. South of Springville large outcrops occur in Shades Valley, and at Trussville are quarries which have supplied the Birmingham furnaces. Analyses 10 to 17, inclusive, Table A, are of material from Trussville; and analyses 12 to 17, inclusive, represent average samples from carload lots delivered to the furnace.

In Murphrees Valley the main outcrop of this rock is on the western side, and quarries at Compton have for many years been worked to supply the Birmingham furnaces. Analyses 18, 19, and 20, Table A, of the rock from these quarries show somewhat varying composition, but by proper selection suitable material could be easily obtained.

In the valleys lying east of Shades Valley and in parts of Shades Valley itself this formation becomes one of prevailing shales and sandstones and the limestones are of limited occurrence and of inferior quality.

Trenton limestone.—The Trenton limestone outcrops in Alabama in three principle areas. In the Tennessee River Valley

some of the smaller streams which flow into the river from the north, like Flint River, Limestone Creek, Elk River, Bluewater Creek, and Shoal Creek, have eroded their valleys into the Trenton limestone. These areas are crossed at only a few points by the railroads leading out from Huntsville and Florence, and no commercial use has yet been made of the rock.

In the narrow anticlinal valleys below enumerated erosion has in most cases sunk the floors of the valleys into Cambrian strata, and, as a consequence, the Trenton limestone occupies a narrow belt on each side, near the base of the Red Mountain ridges. But since a fault usually occurs on one side of these valleys, the Red Mountain ridges and the accompanying Trenton limestone are more fully represented on the unfaulted side, which is the eastern side in all except Murphrees Valley. While the Trenton forms practically a continuous belt along the undisturbed side, extensive areas are sometimes found on the faulted side also. This is the case, for instance, at Vance, on the Alabama Great Southern Railroad, where the rock is quarried for flux for the furnace of the Central Iron Company at Tuscaloosa. Analysis 1 of Table B, shows its composition here. Other series of analyses from lower ledges in the quarry show only 1.22 per cent of silica, but more magnesia.

In cases where erosion has not gone so deep as to reach the Cambrian the Trenton may be found extending entirely across the valleys. This is the case in the lower part of Browns Valley from Brooksville to beyond Guntersville. Above Guntersville the Trenton is seen mainly on the eastern side of the valley. The river touches these outcrops at many points, and at Guntersville the railroad connecting that city with Attalla would afford an additional means of transportation. No developments have yet been made in this area.

The valley separating the Warrior from the Cahaba coal field is known as Roups Valley in the southern and as Jones Valley in the northern part. In these the Trenton occupies a narrow, continuous belt, usually near the base of the eastern Red Mountain ridge, though in places it is high up on the ridge and even at its summit, as at Gate City, where the quarries of the Sloss Iron Company are located. Many analyses of the rock from these quarries have been made, and several are given in Table B, (Nos, 2, 3, 4, 5, 6).

In Murphrees Valley the continuous belt of the Trenton, as above explained, is on the western side, while the faulted remnants are on the eastern side. No quarries have been opened in the Trenton limestone here, but the Louisville and Nashville Railroad goes up the valley as far as Oneonta and would afford means of transportation.

In the Cahaba Valley, which separates the Cahaba coal field from the Coosa coal field, the Trenton is well exposed on the eastern side for the entire length of the valley from Gadsden down. It expands into wide areas near the southern end, where it has been quarried for lime burning, at Pelham, Siluria, Longview, Calera, and other places on the line of the Louisville and Nashville road. Analyses 7, 8 and 9 of Table B, show the composition of the rock in this region.

The Central of Georgia and the Southern railroads cross this belt about midway of its length at Leeds, in Jefferson County, and near its northern end it is crossed by the Louisville and Nashville Railroad, where a quarry at Rock Springs, on the flank of Colvin Mountain, supplies the rock for lime burning. Anaylsis 10 shows the character of the rock at this point.

At Pratts Ferry, on the Cahaba River, a few miles above Centreville, in Bibb County, the Trenton limestone makes high bluffs along the river for several miles, and is in most convenient position for easy quarrying.

Marble works have in former days been established here and should be again put in operation, since the marble is of fine quality and beautifully variegated. No analyses are available, but there is no doubt that much of the rock is sufficiently low in magnesia to be fit for use in cement making. Cahaba River and a short spur from the Mobile and Ohio Railroad would afford transportation facilities for this deposit.

In Big Wills Valley, which separates Sand and Lookout mountains, the Trenton limestone occupies perhaps 25 square miles, but it is crossed only by the railroad connecting Gadsden with Guntersvlile. No anaylses are available.

In the great Coosa Valley region the Trenton outcrops are found mostly on the western border near the base of Lookout Mountain, as in Broomtown Valley, and in other valleys extending south toward Gadsden. While these belts have been utilized in the past for the old Gaylesville, Cornwall, and Round

Mountain furnaces, and possibly for some furnaces now in blast, no analyses are available.

Similarly, farther south, along this western border of the Coosa Valley, and running parallel with the Coosa coal field in Calhoun, St. Clair, and Shelby counties, there are numerous long narrow outcrops of Trenton limestone. The Calcis quarry of the Tennessee Coal, Iron and Railroad Company, on the Central of Georgia Railroad, near Sterritt, is upon one of these outcrops, and furnishes limestone with a very low and uniform percentage of silica and magnesia. Analyses 11, 12, 13, 14, 15, and 16 exhibit the quality of the rock as received at the Ensley Steel Works, but care is taken at the quarry to select ledges low in silica and magnesia, and the analyses therefore represent only the selected ledges and not the average run of the quarry as a whole.

Near Talladega Springs, Marble Valley, and Shelby are other occurrences of the rock, and a quarry a few miles east of Shelby furnace has for many years supplied that furnace with its flux. The quality of the material here is shown by analyses 17, 18, 19, and 20, Table B.

The Cambrian limestones contain generally a very considerable proportion of magnesia, and for this reason are not suited for Portland-cement manufacture, though admirably adapted for furnace stone.

Marbles.—Along the eastern border of the Coosa Valley, near its contact with the metamorphic rocks, there is a belt of limestone which, in places, is a white crystalline marble of great purity, as is shown by analyses 1 to 7, inclusive, of Table C. The Louisville and Nashville Railroad, from Calera to Talladega, passes close to this belt at many points. This marble has been quarried at several places for ornamental stone. It is mentioned here because it is near the railroad and completes the account of the limestone.

THE CLAYS.

The most important clays in the Paleozoic region occur in the Coal Measures, in the Lower Carboniferous, and in the Lower Silurian and Cambrian formations. But, inasmuch as a later formation—the Tuscaloosa of the Cretaceous—borders the Paleozoic on the west and south, and as it contains a great vari-

ety as well as abundance of clays, we shall include it here, although it is not one of the Paleozoics.

Coal Measures.—In this group are numerous beds of shale which have been utilized in the manufacture of vitrified brick and fire brick, but many of them will probably be adapted to cement making. A great body of these shales occurs in connection with the coal seams of the Horse Creek or Mary Lee group, in Jefferson and Walker counties, and in position where they are conventienly situated with reference to limestone and coal and also to transportation lines. They are therefore well worth the attention of those contemplating the location of cement plants.

On the property of Mr. W. H. Graves, near North Birmingham, overlying the coal seam mined by him, there are two beds of shale—one yellowish, the other gray. These two shales have been tested and analyzed, and their composition is shown in Nos. 1 and 2 of the Table D.

Similar shales are known to occur at Coaldale, in Jefferson County, at Pearce's Mills in Marion, and at Cedar Grove Coal Mines in Tuscaloosa. The Coaldale shale is manufactured into vitrified brick. The other two have not yet been utilized.

Analyses 3 and 4 of Table D will show the composition of the shales at Coaldale and Cedar Grove.

It may be of interest to note that Cedar Grove is, so far as yet known, the nearest place to the Gulf ports, where the three essentials in the manufacture of Portland cement, viz., limestone, shale and coal, occur together, and on a railroad.

So also most of the coal seams mined in Alabama rest upon clay beds which have not as yet been specially examined as to their fitness for cement making; but, in view of the proximity of the coal mines to the limestones, it might be worth while to investigate these underclays of the coal seams.

Lower Carboniferous.—Associated with the cherty limestones of the lowermost division of the Lower Carboniferous of some of the anticlinal valleys are beds of clay of excellent quality, much of it being of the nature of china clay.

Probably the best of the exposures of these clays are to be seen in Little Wills Valley, between Fort Payne and the Georgia border, and on the line of the Great Southern Railroad, where for many years quarries have been in operation in sup-

plying the material for tile works and potteries. The clays lie near the base of the formation close above the black shale of the Devonian, and average about 40 feet in thickness, though in places they reach 200 feet. The clay beds alternate with seams of chert which are from 2 to 8 inches in thickness, while the clay beds vary from 12 to 18 inches. The upper half of the clay is more gritty than the lower half which often contains material suitable for the manufacture of the finer grades of porcelain ware. Analyses 5 to 8, in Table D, show the composition of several varieties of clay from this section.

Lower Silurian and Cambrian.—Associated with the cherty limestones and brown iron-ore beds of the formations above named—beds of fine white clay, much of it china clay—are not uncommon. Analysis 9 of the table shows the composition of a white clay from the brown ore bank at Rock Run, in Cherokee County, where the clay is about 30 feet in thickness. Analyses 10 and 11 are also from Rock Run. No. 12, from near Gadsden, No. 13, from Blount County, and No. 14 from Oxanna, in Calhoun County, are clays which seem to be adapted to cement making. While no great number of the clays of these formations have been analyzed, they are known to be widely distributed in Calhoun, Talladega, Jefferson, Tuscaloosa, and other counties in connection with the brown ore deposits.

Cretaceous.—In many respects the most important formation of Alabama, in respect of its clays, is the lowermost division of the Cretaceous, which has been called the Tuscaloosa, and which is in part at least of the same geologic horizon as that of the Raritan clays of New Jersey. The prevailing strata of this formation are yellowish and grayish sands, but subordinated to them are great lenses of massive clay varying in quality from almost pure-white burning clay to dark-purple and mottled varieties high in iron.

The formation occupies a belt of country extending from the north-western corner of the State, around the edges of the Paleozoic formations to the Georgia line at Columbus. Its greatest width is at the northwest boundary of the State where it covers an area 30 or 40 miles wide in Alabama, and of about the same width in Mississippi. The breadth at Wetumpka and thence eastward to the Georgia line is only a few miles. The most important part of this belt is where it is widest in Elmore,

Bibb, Tuscaloosa, Pickens, Fayette, Marion, Lamar, Franklin, and Colbert counties, and the deposits are traversed by the lines of the Mobile and Ohio; the Alabama Great Southern; the Louisville and Nashville; the Southern; and the Kansas City, Memphis and Birmingham railroads; as well as by the Warrior and Tombigbee rivers.

These clays have been described in some detail, and many analyses and physical tests have been presented in the Bulletin No. 6 of the Alabama Geological Survey. From this bulletin have been selected the analyses which appear to indicate the fitness of the clays for cement making.

In Elmore county, in the vicinity of Coosada, along the banks of the river, about Robinson Springs, Edgewood, and Chalk Bluff, there are many occurrences of these clays, some of which have been used in potteries for many years. Analyses 15, from Coosada; 16, from Edgewood; and 17, from Chalk Bluff, are given in the table D.

In Bibb county the clay has been quarried very extensively at Bibbville and near Woodstock for making fire brick. For this purpose the material is carried to Bessemer by the Alabama Great Southern Railroad. No. 18, from Woodstock; and 19, from Bibbville, will represent the average quality of the clay from these beds, which are very extensive, both in thickness and in superficial distribution. The Mobile & Ohio crosses other extensive deposits in the southern part of the county, but no analyses are available.

The most important of the clay beds in Tuscaloosa county are traversed by the Mobile & Ohio Railroad and by the Alabama Great Southern.

Analysis 20, from Hull's; and analysis 21, from the Cribbs beds, are on the Alabama Great Southern; and 22 and 23 are from cuts of the Mobile & Ohio, a few miles west of the city of Tuscaloosa.

Many large beds are exposed along the Mobile & Ohio road in Pickens county also, but very few have been as yet investigated. No. 24 is from Roberts Mill, in this county.

In Lamar and Fayette counties the same conditions prevail as in Pickens and Tuscaloosa. Analysis 25 is of pottery clay from the Cribbs place, in Lamar; and No. 26 is of clay from Wiggins's, 4 miles west of Fayette; and 27 and 28 are clays from W. Doty's place, 14 miles west of that town, in Fayette county.

Marion is one of the banner counties of the State for fine clays, but it is touched by railroads only along its southern border and in the extreme northeastern corner. Although at present not available because inaccessible, the clays mentioned below are worth consideration: No. 29, from Glen Allen; No. 30, from Briggs Fredericks', in Sec. 8, T. 10, R. 13 W. This is from the great clay deposit which gives the name to Chalk Bluff and which underlies about two townships. No. 31 is from a locality about 16 miles southwest of Hamilton, the county seat.

No. 32 is from a locality near the Mississippi line, in section 20, T. 8, R. 15 W., in Franklin county, from land of Mr. Thomas Rollins.

Of the numerous fine clays of Colbert county analyses are given of two from Pegram station, on the Southern Railway, near the Mississippi State line. These are Nos. 33 and 34.

Table A.

Analyses of Lower Carboniferous Limestones.

Number.	1	2	3	4	5	6	7	8	9	10
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	0.50	1.73	0.77	1.14	1.02	1.40	0.68	0.81	0.82	2.16
Iron and alumi-										
num oxide	1.45	.78	.35	.34	1.38	1.17	1.02	.89	.60	2.31
Calcium carb'te.	96.58	96.54	97.60	98.53	95.25	94.67	96.54	97.45	97.37	89.15
Magnesium carbt	2.58	.....	.....	.....	1.73	2.26	1.26	.35	.75	4.20
Sulphur	.....	.....	.....	.....	.....	.....	.....	.....	.029	.....

Number.	11	12	13	14	15	16	17	18	19	20
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	3.12	0.85	1.08	0.73	0.64	1.12	0.42	2.05	4.45	2.80
Iron and alumi-										
num oxide	2.32	.65	.61	.65	.62	.90	.37	.76	3.30	.70
Calcium carb'te.	85.87	96.64	96.91	97.60	97.48	96.38	97.32	89.64	86.35	94.59
Magnesium carbt	4.20	1.36	.90	.52	.76	1.10	1.39	8.15	.....	.....
Sulphur	.....	.024	.019	.018	.....	.....	.020	.....	.....	.....

1. Average sample from Fossick quarry, near Rockwood, Franklin County. Government Arsenal, Watertown, N. Y., analyst.

2. Average sample from Blount Springs quarry—a compact limestone. Henry McCalley, analyst.

3. Average sample from Blount Springs quarry—a granular oolitic limestone. Henry McCalley, analyst.

4. Average sample upper 75 feet, Blount Springs quarry. J. L. Beeson, analyst.

5-9. Average sample Blount Springs quarry. J. R. Harris, analyst.

10, 11. From Worthington quarry, near Trussville, Jefferson county. C. A. Meissner, analyst.

12-17. From Vanns, near Trussville. J. R. Harris, analyst.

18. Average of about 150 feet thickness of rock used for flux, Compton quarry, Blount county. J. L. Beeson, analyst.

19, 20. Stockhouse sample. Compton quarry. Wm. B. Phillips, analyst.

Table B.

Analyses of Trenton Limestones.

Number.	1	2	3	4	5	6	7	8	9	10
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	4.48	5.70	2.43	3.65	3.29	3.82	0.39	0.15	0.78	1.00
Iron and alumi-										
num oxides	1.22	1.87	3.30	.91	1.49	1.96	.13	Tr	.35	.30
Calcium carb'te.	88.85	91.16	89.88	92.38	92.61	90.44	99.11	99.16	97.52	97.00
Magnesium carbt	3.52	.....	.....	.....	.....	.....	.75	.75	1.27	Tr
Sulphur	.....	.....	.....	.....	.....	.....	.....	.....	.....	Tr
Water, organic										
matter and loss	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

Number.	11	12	13	14	15	16	17	18	19	20
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	0.43	0.58	0.38	0.34	0.39	0.98	2.50	2.09	1.08	2.25
Iron and alumi-										
num oxides	.42	.25	.47	.46	.37	.52	1.40	1.01	.63	.68
Calcium carb'te.	98.49	95.78	98.35	96.53	94.27	96.92	96.70	93.77	98.91	95.40
Magnesium carbt	.16	2.89	.30	2.17	4.47	1.08	.....	2.48	.58	.94
Sulphur	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
Water, organic										
matter and loss	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....

1. Average of several carloads flux rock from quarry at Vance, Tuscaloosa county, of Central Iron Company at Tuscaloosa. H. Buel, analyst.

2. Gate City quarry, Jefferson county. Average sample from the crusher. Henry McCalley, analyst.

3-6. Gate City quarry. J. W. Miller, analyst.

7, 8. Longview quarries, Shelby county. Used in lime burning. Report of Alabama State Geologist, 1875.

9. Jones quarry, near Longview. Report of Alabama State Geoligist, 1875

10. Rock Spring quarry, Etowah county. Used in lime burning and for flux. Wm. B. Phillips, analyst.

11-16. Rock from Calcis quarry, St. Clair county. J. R. Harris, analyst.

17-20. Shelby quarry, Shelby county. Used for flux in Shelby furnaces. Report of Alabama State Geologist, 1875.

Table C.

Analyses of Crystalline Marbles.

Number.	1	2	3	4	5	6	7
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	Tr	2.70	2.95	4.65	2.80	1.35	0.28
Iron and aluminum oxides	.....	.40	1.15	.75	.48	.30	.28
Calcium carbnate	99.47	90.80	95.25	94.40	95.60	97.60	99.19
Magnesium carbonate	.38	Tr	.62	.41	.66	Tr	.14

1. Herd's upper quarry, Talladega county. Tuomey's Second Report.
2. Heard's quarry, sec. 16, T. 21, R. 4 E., Talladega county. Wm. B. Phillips, analyst.
3. Taylor's mill, Talladega county, white marble. Wm. C. Stubbs, analyst.
4. Taylor's mill, Talladega county, blue marble. Wm. C. Stubbs, analyst.
5. Taylor's mill, Talladega county. A. F. Brainerd, analyst.
6. Nix quarry, sec. 36, T. 20, R. 4 E., Talladega county, white marble. Wm. B. Phillips, analyst.
7. Gannt's quarry, sec. 2, T. 22, R. 3 E., Talladega county, white marble. A. F. Brainerd, analyst.

Table D.

Analyses of Clays—Paleozoic and Lower Cretaceous.

Number.	1	2	3	4	5	6	7	8	9
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	61.55	57.80	57.22	58.50	79.80	82.04	66.25	82.11	60.50
Alumina	20.25	25.00	24.72	18.28	11.75	12.17	22.90	11.41	26.55
Ferric oxide	7.23	4.00	7.14	10.22	1.75	Tr	1.60	1.40	.30
Lime	Tr	2.10	.49	1.19	.75	Tr	Tr	Tr	.90
Magnesia	.99	.80	1.88	1.40	Tr	.33	Tr	.66	.65
Alkalies	1.25	1.80	.40	.70	1.50	.60	.75	1.80	2.70
Ignition	6.19	7.50	7.09		4.11	4.33	9.05	4.00	7.90
	98.66	99.00	98.93	.....	99.16	99.47	100.55	101.38	99.50

Number.	10	11	12	13	14	15	16	17	18
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	72.20	57.00	67.95	61.50	84.21	66.61	62.60	60.38	65.82
Alumina	22.04	17.80	20.15	26.20	9.75	21.04	26.98	20.21	24.58
Ferric oxide	.16	5.60	1.00	2.10	.69	2.88	.72	6.16	1.25
Lime	.50	2.10	1.00	.50	.70	.40	.40	.09	.....
Magnesia	.40	1.20	Tr	.43	.14	.58	.36	.72	Tr
Alkalies	.60	6.00	1.87	.70	....	.70	.65	1.80	.60
Ignition	5.80	9.45	8.00	7.29	4.10	7.00	9.30	10.21	8.16
	101.70	99.15	99.97	98.72	99.59	99.21	101.01	99.57	100.41

Number.	19	20	21	22	23	24	25	26	27
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct
Silica	74.25	61.25	65.35	60.03	58.13	68.23	60.90	63.27	67.10
Alumia	17.25	25.60	21.30	24.66	24.68	20.35	18.98	19.68	19.37
Ferric oxide	1.19	2.10	2.72	3.69	3.85	3.20	7.68	3.52	2.88
Lime	.40	.25	.60	.13	.15	.34	Tr	1.30	Tr
Magnesia	Tr	.82	.86	.38	.32	Tr	Tr	Tr	.73
Alkalies	.52	1.35	Tr	Tr	1.78	.74	Tr	1.20	.67
Ignition	6.30	8.10	8.79	11.34	11.78	7.16	13.36	9.80	7.79
	99.39	99.47	99.62	100.23	100.51	100.02	100.92	98.77	98.54

Number.	28	29	30	31	32	33	34		
	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct	Pr ct		
Silica	65.58	68.10	65.49	70.00	67.50	66.45	64.90		
Alumina	19.23	21.89	24.84	21.31	19.84	18.53	25.25		
Ferric oxide	4.48	2.01	Tr	2.88	6.15	2.40	Tr		
Lime	Tr	.80	1.26	.20	.12	1.50	Tr		
Magnesia	Tr	.28	Tr	Tr	.10	1.25	Tr		
Alkalies	....	.40	Tr	Tr	....	Tr	....		
Ignition	6.90	5.75	7.80	6.85	7.65	9.46	8.90		
	96.19	99.23	99.39	101.24	101.36	99.59	99.05		

Coal Measures..
1. Dark yellow shale from Coal Measures, W. H. Graves, near Birmingham, Jefferson county.
2. Light gray shale from same locality.
3. Shale from Coaldale, Jefferson county. Analysis by F. W. Miller.
4. Shale over coal seam, Cedar Grove Coal Mines, near Vance, Tuscaloosa county.

Lower Carboniferous
5-7 Fire clay, near Valley Head, DeKalb county.
8. China clay, Eureka mines, DeKalb county.

Silurian and Cambrian.	9.	China clay, Rock Run, Cherokee county (Dyke's ore bank.)
	10.	Fire clay, Rock Run, Cherokee county.
	11.	Pottery clay, Rock Run, Cherokee county.
	12.	China clay, J. R. Hughes, Gadsden, Etowah county.
	13.	Stoneware clay, Blount county.
	14.	Stevens, Fire clay, Oxanna, Calhoun county; probbably too much free sand.
Lower Cretaceous (Tuscaloosa)	15.	Stoneware clay, Coosada, Elmore county.
	16.	Pottery clay, McLean's, near Edgewood, Elmore co.
	17.	Stoneware clay, Chalk Bluff, Elmore county.
	18.	Fire clay, Woodstock, Bibb county.
	19.	Fore clay, Bibbville, Bibb county.
	20.	Fire clay, Hulls Sta'n., A. G. So. R. R. Tuscaloosa co.
	21.	Pottery clay, H. H. Cribbs, A. G. So. R. R., Tuscaloosa county.
	22.	Pottery clay, J. C. Bean, M. & O. R. R., Tuscaloosa co.
	23.	Fire clay, J. C. Bean, M. & O. R. R., Tuscaloosa co.
	24.	Stoneware clay, Roberts' Mill, Pickens county.
	25.	Pottery clay, Cribbs' place, Lamar county.
	26.	Stoneware clay, H. Wiggins, Fayette county.
	27-28.	Pottery clay, W. Doty, Fayette county.
	29.	Blue clay, R. R. cut, near Glen Allen, Marion county.
	30.	China clay, Briggs Frederick, Marion county.
	31.	Pottery clay, 10 miles S. W. Hamilton, Marion co.
	32.	Pottery clay, Thos. Rollins, Franklin county.
	33.	Pottery clay, J. W. Williams, Pegram, Colbert co.
	34.	China clay, Pegram, Colbert county.

CHAPTER II.

THE PORTLAND CEMENT MATERIALS OF CENTRAL AND SOUTHERN ALABAMA.

The raw materials suitable for the manufacture of Portland cement, which occur in Central and Southern Alabama, are argillaceous limestones, purer limestones, and clays.

The limestones valuable as cement materials occur mainly at two horizons, viz., in the Selma chalk or Rotten limestone of the Cretaceous, and in the St. Stephens formation of the Tertiary. The clays available are residual clays from the decomposition of the two limestone formations above mentioned, the stratified clays of the Grand Gulf formation, and alluvial clays occurring in the river and creek bottoms. It is further possible that later investigation may show that some of the other stratified clays of the Tertiary formations are suitable, and this is especially likely to be the case with the clays of the lowermost Cretaceous or Tuscaloosa formation.

THE SELMA CHALK OR ROTTEN LIMESTONE.

Geological horizon.—The Cretaceous system in Alabama is susceptible of classification into four divisions, which are, in ascending order,

1, the Tuscaloosa, a formation of fresh-water origin, made up in the main of sands and clays in many alterations. In places the clays occur in deposits of sufficient size and of such a degree of purity as to make them of commercial value.

2, the Eutaw, which is of marine origin and composed of sands and clays more or less calcareous, but nowhere showing beds of limestone properly so called.

3, the Selma chalk, which is of marine origin, and is composed, in part at least, of the microscopic shells of Foraminifera. This formation, throughout the western part of the belt covered by it in Alabama, is about 1,000 feet in thickness, and is made up of beds of chalky and more or less argillaceous limestone. In a general way it

may be said that the lower and upper thirds of the formation contain 25 per cent. and upward of clayey matters mixed with the calcareous material, while the middle third will hold less than 25 per cent. of these clayey impurities.

4, the Ripley. This, like the preceding, is a marine formation, in which, generally, the calcareous constituents predominate, but in places it contains sandy and clayey beds.

From this summary it will be seen that the Selma chalk is the one of Cretaceous formations in Alabama which offers limestone in such quantity and of such composition as to be fit for Portland cement material.

General description.—As has been stated above, the Selma chalk is a calcareous formation throughout its entire thickness of about 1,000 feet. The rock, however, varies in composition between somewhat wide limits, and taking account of the composition we may readily distinguish three divisions of it. The rock of the upper or Portland division is highly argillaceous, holding from 25 per cent. and upward of clayey matters; portions of it are composed of calcareous clays or marls rather than limestone, and in these beds are found great numbers of fossils, mainly oysters. Along Tombigbee River these beds make the bluffs from Pace's Landing down nearly to Moscow, and on the Alabama they form the banks of the river from Elm Bluff down to Old Lexington Landing. The strata, as exhibited in these bluffs, consist of dark-colored, fossiliferous, calcareous clays, alternating with lighter-colored and somewhat more indurated ledges of purer, less argillaceous rock. At Elm Bluff, which is about 125 feet high, the upper half of the bluff is of this character. The lower half of the bluff is composed of rock more uniform in composition and freer from clay, and is the top of the middle part of the Selma formation (the Demopolis division), which is made up of limestone of more uniform character, containing, generally, less than 25 per cent. of clayey material.

In this middle or Demopolis division of the Selma formation the fossils are rarer than in either of the others, oysters and anomias being the most common forms. This variety of the rock forms the bluffs along Alabama River from Elm Bluff up to King's Landing. It is seen in its most typical exposure at White Bluff, where it is at least 200 feet in thickness, and

makes on the right bank of the river an almost perpendicular bluff. On Tombigbee River it extends from near Barton's Bluff past Demopolis up to Arcola and Hatch's Bluff. Its lowermost beds, a compact limestone of great purity, form the upper parts of Barton's and Hatch's Bluffs. On Little Tombigbee River the same rock makes the celebrated bluffs at Bluffport and at Jones Bluff (Epes), beyond which for several miles it is shown along the stream.

Judging from the width of its outcrop, this division of the Rotten limestone must be about 300 feet in thickness. It underlies the most fertile and typical "prairie" lands of the South. At intervals throughout this region the limestone rock appears at the surface in what are known as "bald prairies," so named from the circumstance that on these spots there is no tree growth. The disintegration and leaching out of the limestone leaves a residue of yellowish clay, which accumulates sometimes to a thickness of several feet in low places. This clay is used at the Demopolis plant in the manufacture of cement, and in most localities where suitable limestone is found the clay is present in sufficient quantity to supply the needs of the cement manufacturer.

At the base of this middle or Demopolis division occurs a bed consisting of several ledges of compact, hard, pure limestone, which weathers into curious shapes, and has received the names horse-bone rock and bored rock. This bed, as above mentioned, appears at the top of Hatch's Bluff; also at Arcola Bluff, and between Demopolis and Epes, at Jordan's Ferry, and other places. Where it outcrops across the country it makes a ridge easily followed and characterized by the presence on the surface of loose fragments of the limestone.

The lower part of the formation (the Selma division), like the upper, is composed of clayey limestone, in many places being rather a calcareous clay. The color is dark gray to bluish, and in most exposures there is a striping due to bands of light-colored, purer limestone alternating with the prevailing quality. Along Alabama River the strata of this division are seen in the bluffs from King's Landing up to Selma and beyond. On the Warrior River they are seen in the bluffs at Arcola, Hatch's, Millwood, and Erie, occupying in the last-named locality the upper part only of the bluff. On the Tombigbee, the bluffs at Gainesville, at Roe's, and Kirkpatrick's are formed mainly of

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Plate II.—Caves in Limestone, below Roe's Bluff, Tombigbee River.

the rocks of this division, while above Roe's, at Jordan's, occurs the line of junction of this with the middle division. Near this line of division there is a very characteristic feature to be observed at many points, viz., about 10 or 15 feet below the hard ledges of pure limestone forming the base of the middle (Demopolis) division the dark-colored argillaceous rock shows a tendency to flake off and weather into caves, sometimes to be seen for long distances along the bluffs, as on Alabama River just above King's Landing, on the Tombigbee below Roe's Bluff, and at Jordan's Ferry. This peculiarity is illustrated in Plate II. The outcrop of the argillaceous rocks of this division gives rise to black prairie soils, in which beds of fossil shells, mainly oysters, are common.

It has been suggested that the argillaceous rocks of this and the uppermost division could be mixed with the purer limestone of the middle division in such proportions as to constitute a good cement mixture. In this case it would be easy to select localities near the junction of the two divisions where both varieties of the rock could be quarried, if not in the same pits, at least in pits closely adjacent. This would do away with the need of adding other clay to the limestone. Localities of this sort would be found along the border north and south of the belt of outcrop of the white Demopolis rock.

Details of localities.—The general characters of the rock of this formation have been mentioned above, and it remains to give details of the special localities examined, together with analyses of the limestones collected. In making the collections material from the middle or Demopolis division of the formation has been generally chosen, since most of the limestone of the formation which contains 75 per cent. and upward of carbonate of lime is to be found in this division. At the same time specimens of the more argillaceous material, especially of the lower (Selma) division of the formation, have been taken for comparison and analysis, with a view to ascertaining whether or not it will be practicable to provide a cement mixture by using the proper proportions of the purer and more argillaceous materials.

Inasmuch as suitable material for cement manufacture can be had in practically unlimited quantity all along the outcrop of the pure limestone of the Demopolis division, the location of the plants for the manufacture of this product will be determined by

other considerations than the quality of the rock. Chief among these will be the facilities for transportation, cheapness of fuel, cost of labor and abundance of it at command.

Examinations have consequently been confined to those localities which appear to be most favorably situated in these respects, and especially to those localities which are on navigable streams or on north-south railroad lines, or on both.

The first place considered on Tombigbee River is Gainesville, where the limestone appears on the river bluff in a thickness of 30 to 40 feet, beneath a heavy covering of Lafayette sands and pebbles. (Plate III.) A short distance inland from the river, however, the rock appears at the surface, and may be quarried without difficulty. Specimens have been taken from the different parts of the bluff near the ferry, which will show the composition of the limestone here (see analyses 1, 2, 3, and 4, Table E). Other specimens are from the Roberts place, 3 miles east of Gainesville—one of which was taken from the top of a 30-foot bluff; others from the surface 1 mile and 5 miles from the river (analyses 5 and 6.)

At Jones' Bluff, on the Tombigbee, near Epes station, on the Alabama Great Southern Railroad, the white limestone of remarkably uniform composition shows along the river bank for a distance of a mile or so, with an average height of perhaps 60 feet. (Plate IV.) Here the bare rock forms the surface, so that there would be no overburden to be removed in quarrying. The railroad crosses the river at this locality, which thus has the advantage of both rail and water transportation. From the lower end of this exposure down to Bluffport the white rock is seen at many points, e. g., below Lees Island, Hillman's (Plate V), Martin's Ferry, Braggs, etc. It generally has a capping of 15 to 20 feet of red loam and other loose materials.

Specimens have been analyzed from Epes and Hillmans (analyses 7, 8 and 9, Table E.)

At Bluffport (Plate VI) the white rock in places forms a bluff 100 feet or more in height along the right bank of the river for a distance of a mile or more. This is the counterpart of Jones' bluff, above mentioned, and the character of the material is shown by analysis No. 10. As at Epes, the rock extends up to the surface, so that the quarrying would be attended with little or no difficulty. Below the Bluffport bluffs the easterly course of the river brings it into the territory of the lower

Plate III.– Gainesville, Tombigbee River.

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Plate IV.—Jones' Bluff, Tombigbee River, at Epps, looking down stream from bridge.

Plate V.—Hilman's Bluff, below Epes, Tombigbee River.

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Plate VI.--Chalk exposure at Bluffport, Tombigbee River.

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Plate VII.—Below Jordan's Ferry, Tombigbee River.

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Plate VIII.—Roe's Bluff, Tombigbee River.

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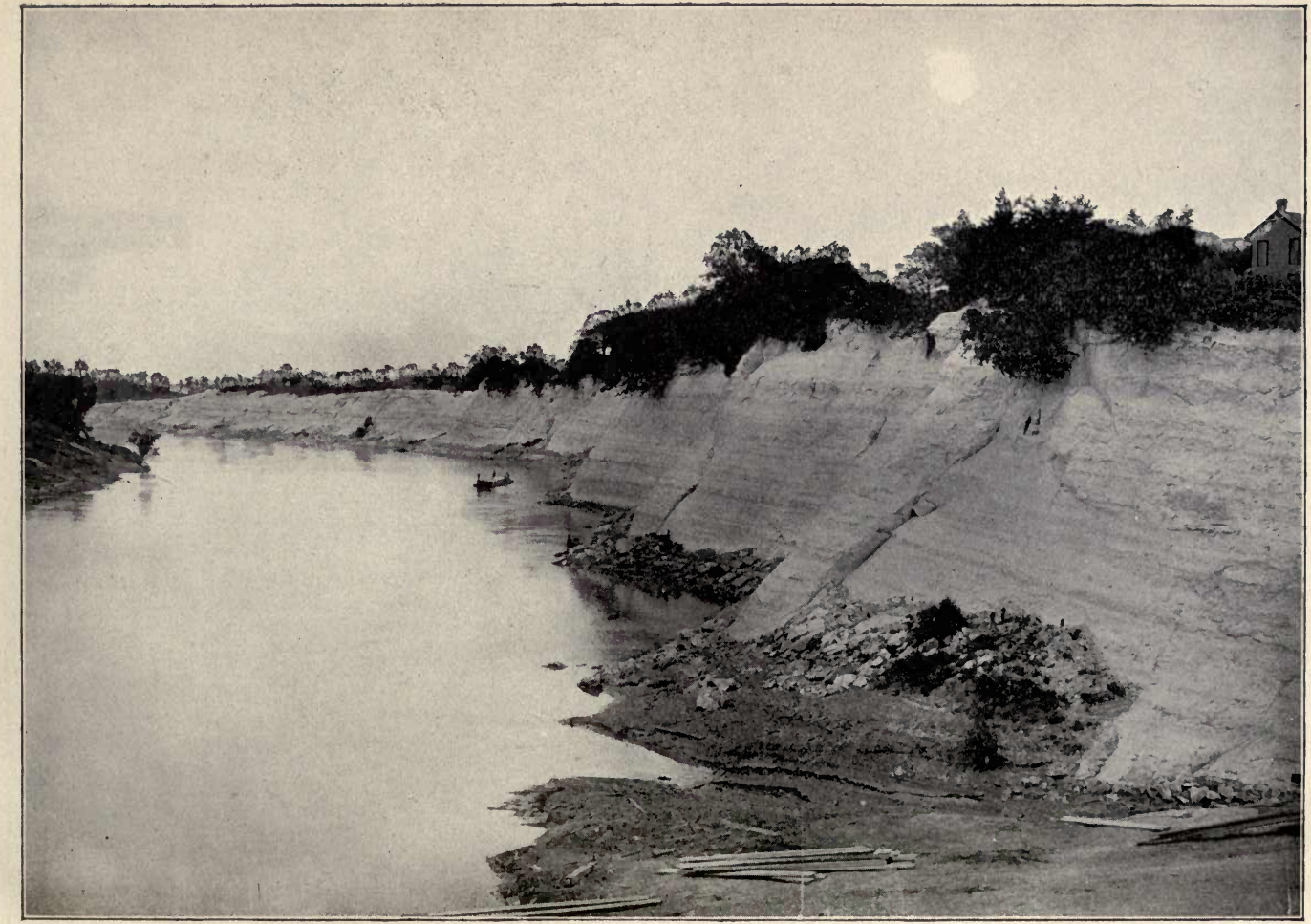

Plate IX—Bluff of Selma Chalk, Demopolis, Tombigbee River, looking up stream from Steamboat Landing.

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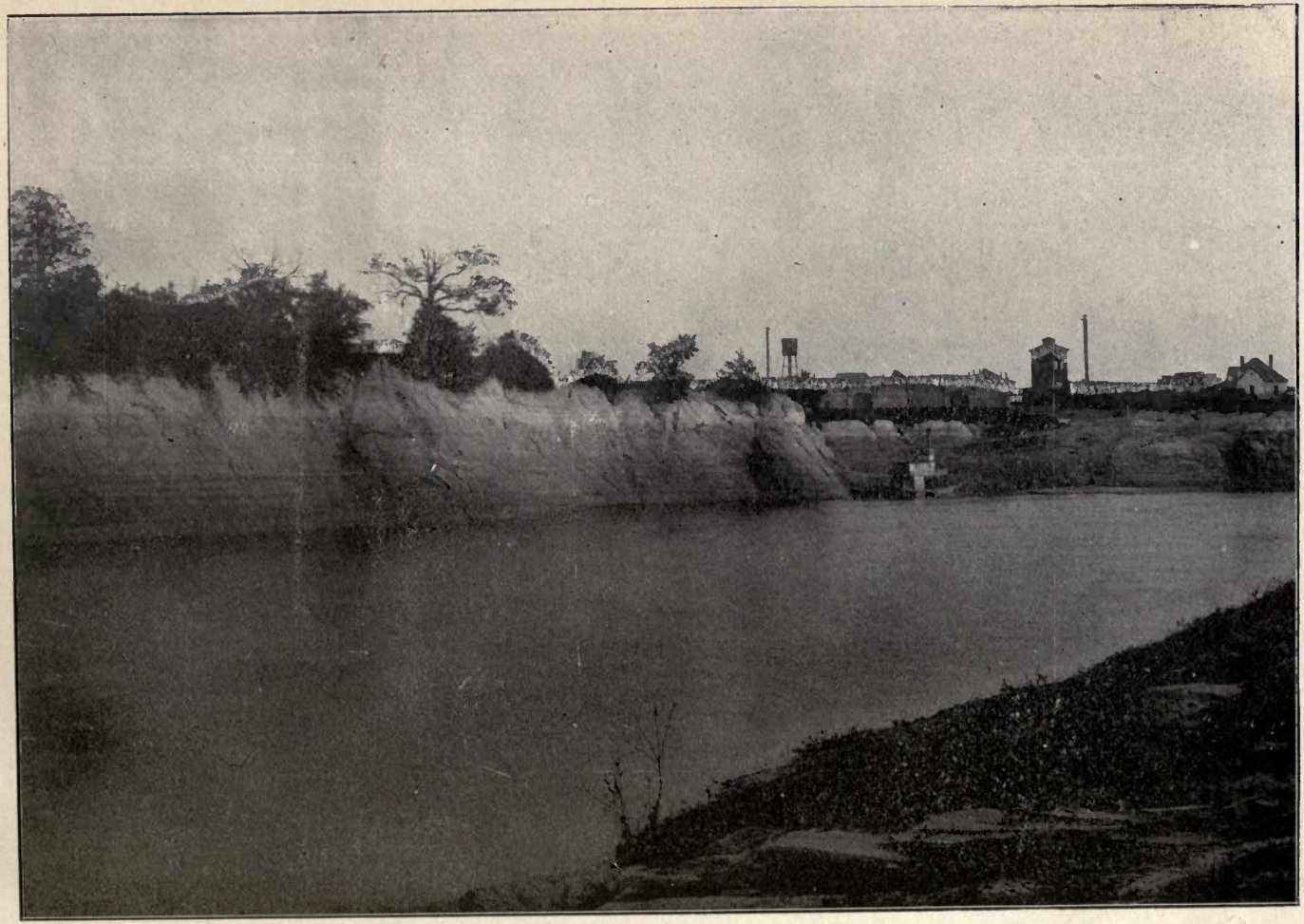

Plate X—Bluff at Demopolis, Tombigbee River, looking down stream Alabama River.

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Plate XI.—Hatch's Bluff, above Demopolis, on Warrior River.

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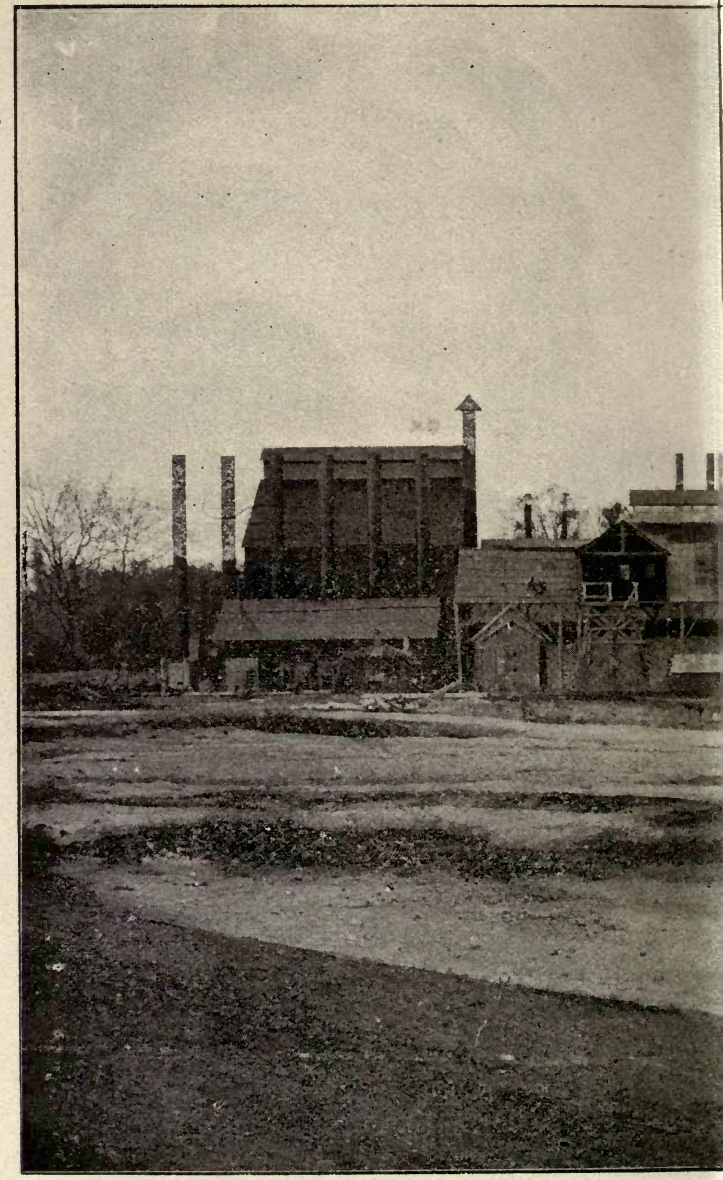
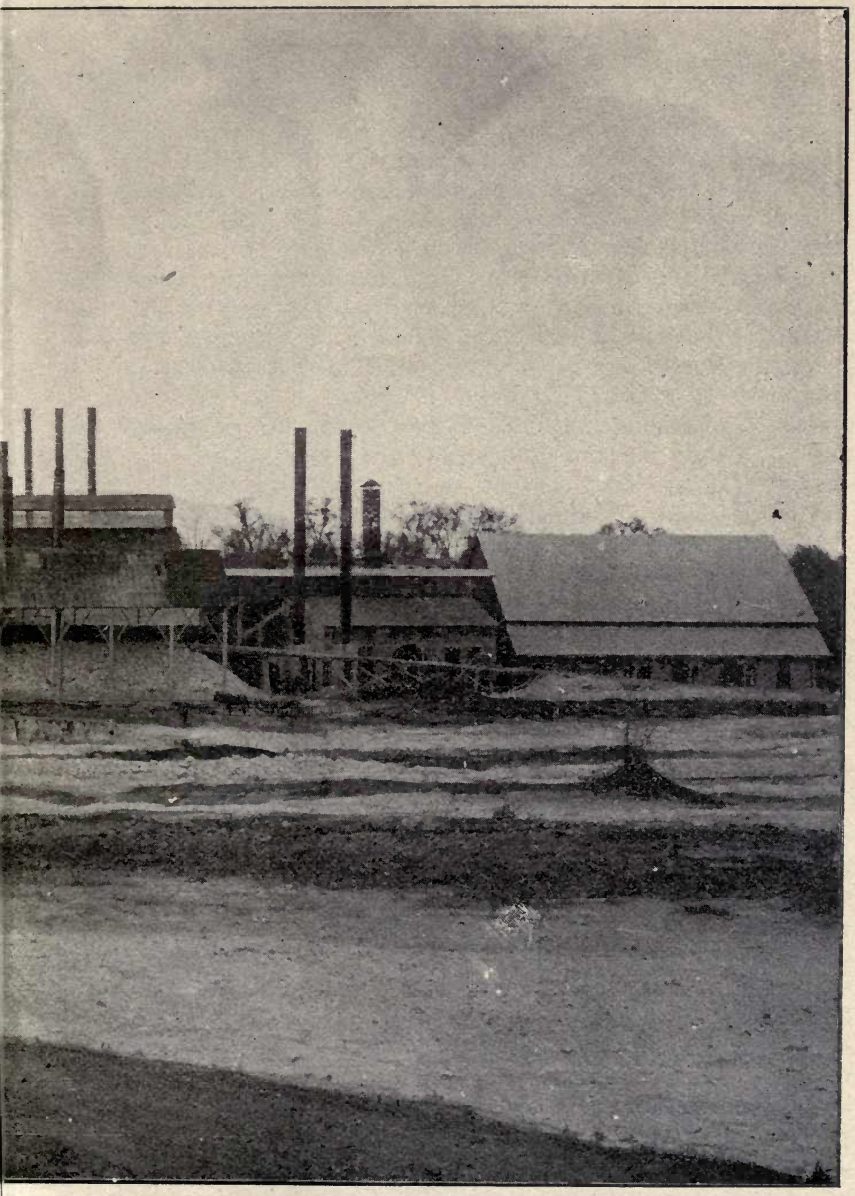


Plate XII.—Alabama Po



nd Cement Works, at Demopolis.

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strata of the formation, and we do not see the white rock again below Jordan's Ferry, (Plate VII) except in thin patches at tops of some of the bluffs. The character of the material of these lower beds may be seen from the analyses of specimens taken from Jordans and Belmont and Roe's bluff, Nos. 11, 12, 13, and 14. The two specimens from the last-named locality represent the composition of the prevailing dark-colored argillaceous rock and of the lighter-colored ledges. (Plate VIII.)

At Demopolis there is an important occurrence of the white rock extending along the left bank from a mile above the landing to about 2 miles below, with an average height perhaps of 40 or 50 feet. (Plates IX and X.) The rock is remarkably uniform in appearance and probably in composition (analysis 17.) At McDowell's the main bluff is on the right bank and the rock is of great purity, as shown by analysis 16. The exposures continue down to Pace's Landing, 9 miles below Demopolis, and beyond this the bluffs are much darker in color and striped with lighter bands, characteristic of the strata of the upper part of the formation. Thence down nearly to Moscow occur the exposures of these upper beds.

Above Demopolis at Arcola and Hatch's bluff the bluish clayey limestones of the Selma division are seen in force, with the lowermost ledges of the Demopolis division—the horsebone rock—capping them. Two analyses of these varieties at Hatches will show well the contrast in their chemical composition (analyses 19 and 20. (Plate XI.)

From Demopolis eastward the line of the Southern Railway is located on the outcrop of this white rock, at least as far as Massillon, where it passes into the territory of the lower Selma division. Two miles from Demopolis on this road is the cement manufacturing plant of the Alabama Portland Cement Company, with six kilns in place. The quarry is on the opposite side of the railroad track from the kilns, but only a few hundred feet distant. (This plant with quarry in the foreground is shown in Plate XII.) The clay used is the residual clay from the decomposition of the limestone, and is obtained from the river bank a few yards away. The composition of the rock and of the clay used in the manufacture is shown by analyses 15, 18, and 31, Table E, and 1, Table G. A specimen taken from Knox wood station, between the cement works and Demopolis station, shows similar composition. The analyses below given (10, 11,

12 of Table G) show the chemical character of the cement manufactured at Demopolis.

At Van Dorn station the white rock outcrops in the fields over considerable territory, (Plate XIII), and just east of the station there is a deep cut through it. Analyses from about Van Dorn show sufficiently well the character of the material at these points (analyses 21 and 22 of Table E.)

About Uniontown the bare rock is exposed at numerous points, and the advantages of this place for the location of manufacturing plants seem to be very great. Specimens have been taken from the Bradfield and Shields places, west of the town, and from the Pitts place east, and from a point south of the town along the McKinley road. Other specimens have come from plantations near the road for several miles eastward and the analyses are appended (analyses 23, 24, 25, 26, 27 and

The composition of the residual clay overlying the limestone at the Pitts place is shown in analysis No. 2 of Table G, and that of a similar clay from the "Graveyard Hill" on the Morgan place, by analysis No. 3 of same table.

South of Massillon, near the crossing of the Southern and Louisville and Nashville railroads, in the vicinity of Martin's station, the white rock shows in numerous exposures through the fields, making a country somewhat similar to that about Uniontown. At many points the rock has no overburden, and is admirably adapted to cheap quarrying. On the banks of Bogue Chitto Creek, near Martin's station, on the Milhous place, the rock is exposed in a bluff with a bed of plastic clay overlying, but here it is below a considerable thickness of red loam and sands of the Lafayette formation. The character of the rock at Milhous station, west of Martin's, may be seen from the analysis No. 29, Table E.

The same rocks make the great bluff of White Bluff, on Alabama River, (Plate XIV.) Specimens were selected from this bluff at two points—one about halfway down the bluff, the other twenty feet lower. Generally there is a capping of the red loam and sands of the Lafayette over the limestone, but near the upper end of the bluff the white rock extends to the summit, where it has a capping of plastic clay only. The charaster of the limestone from this locality is shown in analysis 30, Table E, and that of the overlying residual clay in analysis 4 of Table G.

At Elm Bluff, as has already been shown, the upper and middle divisions of the formation are in contact. (Plate XV.)

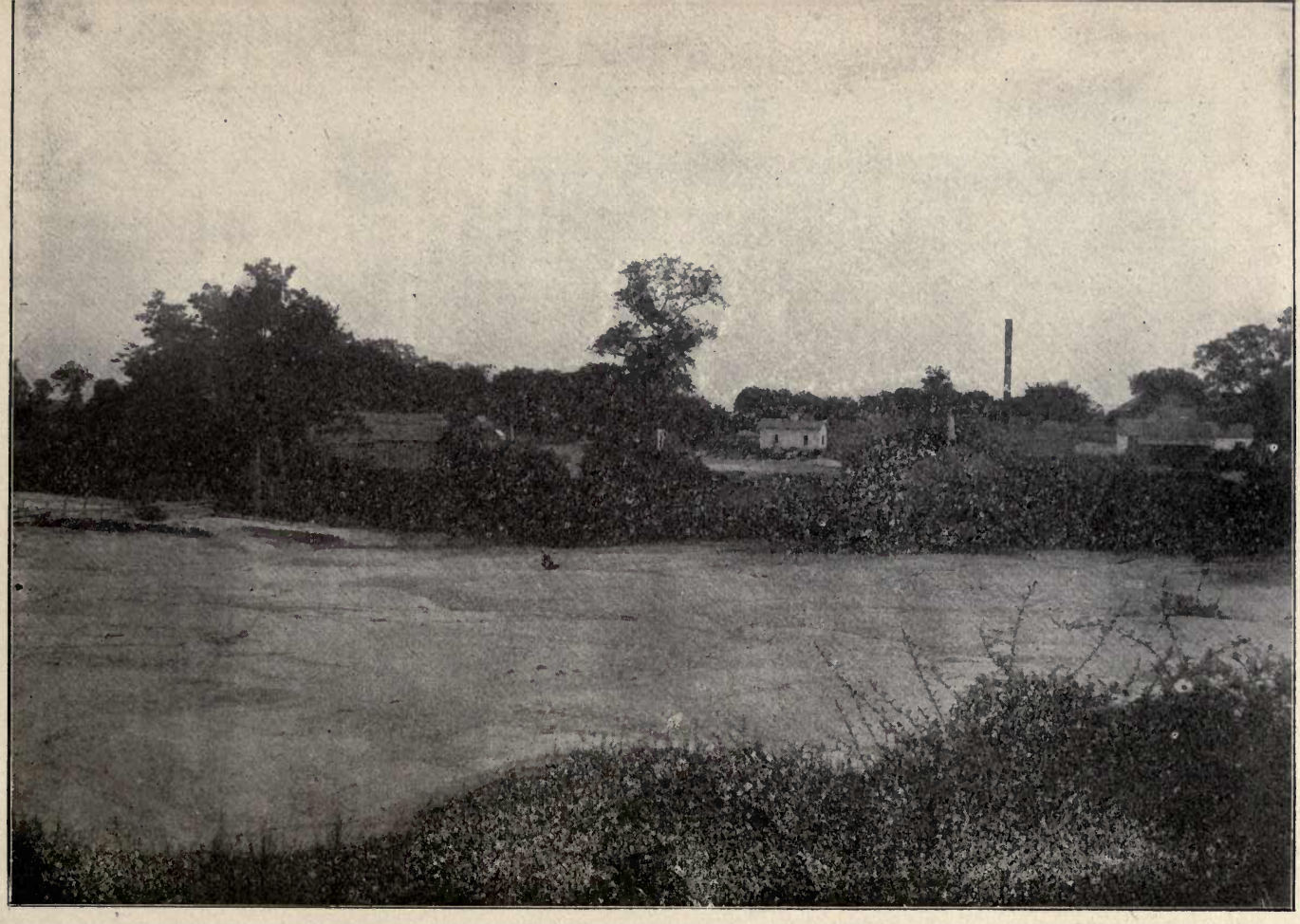

Plate XIII.—Exposure of Selma Chalk at VanDorn's Station, Marengo County.

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Plate XIV.—White Bluff, Alabama River.

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Plate XV.—Elm Bluff, Alabama River.

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At King's Bluff the middle and lower parts of the formation are in contact. At the other bluffs of the river between King's Landing and Selma the rock of the lower division is exhibited. No. 32 (Table E) is of the rock at the steamboat landing in Selma; No. 33 of rock occurring near Selma; No. 34 from Cahaba; and No. 35 from Benton.

These analyses show that the rock of this division is in general too clayey for the best cement rock, but it might be mixed with the purer limestone of Uniontown, or Demopolis in making up a cement mixture.

To summarize: From Demopolis eastward along the line of the Southern Railway, by Van Dorn, Gallion, Uniontown, Massillon, and thence by Martins and Milhous stations to White Bluff, the white or Demopolis type of rock appears at the surface in clean exposures at almost innumerable points, either immediately on the railroad or at very short distance from it. So far as the quality, quantity, and accessibility of the limestone rock are concerned, manufactories of cement might be located almost anywhere in this territory. From Demopolis westward the same conditions prevail up the river to Epes, and thence to Gainesville, beyond which point the white rock is to the west of the river at greater or less distance.

East of Alabama River the outcrop of the cement rock is crossed by the Louisville and Nashville Railroad (Repton branch), as before stated, between Berlin and Pleasant Hill stations. At Benton, on Alabama River, and on the railroad, the limestone has the composition shown by analysis 35.

On the Montgomery and Selma road, at the crossing of Pintlala Creek near Manack station, the limestone is exposed in the creek banks and in the open fields, often with little or no overburden. In Table E are given analyses of a specimen from the fields along the wagon road (No. 36), and from the creek bank (No. 37.)

On the main branch of the Louisville and Nashville Railroad the white rock shows between the city and McGhees switch, and an analysis of a specimen from McGhees is given (No. 38.) Somewhat similar, but rather better, is the limestone from H. A. Jones, 8 miles south of Montgomery, shown in analysis No. 39.

Examinations have not been carried beyond Montgomery, but it is known that the white prairie rock is crossed by the Central of Georgia Railroad between Matthews and Fitzpatrick stations, and there seems to be no doubt that along this stretch of the road suitable rock will be found convenient to the line.

Table E.

Analyses of Crateceous Limestones.

Locality.	Silica.	Iron and aluminum oxides.	Calcium carbonate.	Magnesium carbonate.	Sulphuric anhydride.	Total sulphur.	Water and organic matter.
1 Gainesville Bluff, Tombigbee river, 5 feet from top of bluff; R. S. Hodges, analyst	18.46	16.04	56.71	1.69	1.32	.....	5.78
2 Gainesville Bluff, Tombigbee river, lower part of bluff; R. H. Hodges, analyst	14.50	11.64	67.67	2.26	1.97	.....	1.96
3 Gainesville limestone; F. P. Dewey, analyst	18.42	10.79	65.21	1.57	.30	0.83	.....
4 Gainesville limestone; A. W. Dow, analyst	27.25	15.96	54.00	1.11	.44	1.23	.....
5 Robert's place, near Gainesville, top of bluff; R. S. Hodges	12.10	10.70	75.57	1.24	.69	.....	1.70
6 Robert's place near Gainesville, 5 feet above water; R. S. Hodges	14.28	11.80	69.75	1.50	1.02	.....	1.65
7 Jones Bluff, at Epes; R. S. Hodges	4.78	6.42	86.28	1.02	.....	.....	1.30
8 Jones Bluff, at Epes; Dr. Mallett	3.23	3.96	80.48	.53	.....	.....	2.22
9 Hillmans Bluff, below Epes; R. S. Hodges	10.08	9.47	77.43	1.30	.....	.....	1.99
10 Bluffport ferry, Tombigbee river; R. S. Hodges	8.10	5.40	85.10	1.25	.....	.....	.....
11 Jordans ferry, Tombigbee river; R. S. Hodges	.....	.....	67.28	1.87	.....	.....	1.53
12 Belmont Bluff, Tombigbee river; R. S. Hodges	21.00	15.60	55.84	2.12	.....	.....	5.44
13 Roes Bluff, Tombigbee river, main part of bluff; R. S. Hodges	20.40	15.76	55.82	2.10	.....	.....	5.92
14 Roes Bluff, Tombigbee river, light-colored ledges; R. S. Hodges	9.68	8.70	78.52	1.02	.....	.....	2.08
15 Demopolis limestone, F. P. Dewey; U. S. Mint, analyst	13.32	7.74	73.94	1.40	.27	.64	.....
16 McDowells Bluff, below Demopolis; R. S. Hodges	3.82	3.86	90.40	1.15	.....	.....	.77
17 Demopolis limestone; Dr. J. W. Mallett, analyst	12.13	7.45	77.69	.72	.....	.....	2.49
18 Material used in Demopolis Cemen Wks; R. S. Hodges, analyst.	7.64	7.62	80.71	1.05	1.62	.....	1.36
19 Hatch's Bluff, Warrior river above Demopolis; main part of bluff; R. S. Hodges	25.90	19.44	44.78	2.68	.....	.....	7.20
20 Hatch's Bluff, Warrior river above Demopolis; ledges at top of bluff; R. S. Hodges	1.78	2.34	93.52	1.38	.....	.....	.98

Analyses of Crateceous Limestones.—Continued.

Locality.	Silica.	Iron and aluminum oxides.	Calcium carbonate.	Magnesium carbonate.	Sulphuric anhydride.	Total sulphur.	Water and organic matter.
21 At VanDorn station, from roadside; R. S. Hodges	8.90	8.26	80.47	1.30	.....	.....	1.07
22 At VanDorn station, railroad cut east of station; R. S. Hodges	9.80	7.85	78.77	1.04	.....	.....	2.54
23 Uniontown, P. H. Pitt's Home place; R. S. Hodges	10.86	8.40	75.35	1.35	.....	.....	4.04
24 Uniontown, P. H. Pitts, Houston place; R. S. Hodges	13.58	9.20	72.21	1.98	.....	.....	3.03
25 Uniontown, P. H. Pitts, Rural Hill place; R. S. Hodges	12.10	9.80	74.52	1.17	.....	.....	2.41
26 Uniontown, 1 mile south on McKinley road; R. S. Hodges	7.56	7.18	83.45	1.53	.....	.....	.....
27 Uniontown, Bradfield place; R. S. Hodges	17.77	9.24	65.96	1.52	.....	.....	5.51
28 Uniontown, Shields place; R. S. Hodges	19.62	11.71	62.81	2.04	.....	.....	2.49
29 R. R. cut, Milhous station, So. Ry. Dallas county; R. S. Hodges	10.50	7.24	80.10	.98	.....	.....	1.18
30 White Bluff, Alabama river, lower part of bluff; R. S. Hodges	17.44	11.48	64.35	1.61	.....	.....	5.22
31 Limestone used in cement works, Demopolis; analysis furnished by T. G. Cairns	9.88	6.20	77.12	1.08	.....	.....	5.72
32 Limestone from bluff at steamboat landing, Selma; F. W. Miller, analyst	16.11	11.22	65.08	2.42	1.40	.....	3.37
33 Near Selma, white rock; O. M. Cawthon, R. S. Hodges	18.66	13.42	64.10	2.58	.08	.....	1.16
34 Limestone from Cahaba, Alabama river; Dr. Mallet	19.64	9.40	65.81	.79	.....	.....	3.58
35 Limestone from Benton, Alabama river; Dr. W. B. Phillips	19.74	11.67	54.83	5.14	.85	.....	4.96
36 Limestone from Manack station, Lowndes county; R. S. Hodges	13.50	11.46	67.16	1.08	1.01	.....	5.79
37 Limestone, Manack station; Dr. B. B. Ross, analyst	13.20	9.00	74.26	1.46	.....	.....	.....
38 Limestone, McGhee's Switch, Montgomery co.; R. S. Hodges	21.98	14.78	54.67	1.39	.11	.....	7.07
39 Limestone, H. A. Jones, 8 miles S. of Montgomery; R. S. Hodges	14.90	14.34	63.28	1.47	.....	.....	6.01

THE ST. STEPHENS LIMESTONE.

General Description.—The St. Stephens or White limestone formation of the Alabama Tertiary, which includes the uppermost of the Eocene strata, is in general equivalent to the Vicksburg limestone of the Mississippi geologists.

In Alabama it exhibits three rather well-defined phases, which in descending order are (1) the Upper or Salt Mountain division, observed at one locality only in Clarke county; (2) the Middle or St. Stephens division, and (3) the Lower or Jackson division. Of these it is only the middle division with which we are here concerned, since the first is, so far as known, restricted to one locality, and the third is seldom exposed along Alabama rivers and railroads.

The following section of the St. Stephens Bluff, Tombigbee River, (Plate VI), will give an idea of the strata of this division:

Section of St. Stephens Bluff.

	Feet.
1. Red residual clay	1 to 5
2. Highly fossiliferous limestone holding mainly oysters, and full of holes, due to unequal weathering	10 to 12
3. Orbitoidal limestone (chimney rock), a soft, nearly uniform porous limestone, making smooth perpendicular face of the bluff except where bands of harder limestone of very nearly similar composition alternate with the softer rock. Both varieties hold great numbers of the circular shells of *Orbitoides mantelli.* These harder ledges are nearly pure carbonate of lime, take a good polish, and are often burned for lime.....	60
4. Immediately below 3, for 5 or 6 feet, the strata were not visible, being hidden by the rock falling from above, but the space seems to be occupied by a bluish clay. Then follows a soft rock somewhat of same consistency as No. 3 above, but containing a good deal of green sand. The fossils are mostly oysters and *Plagiostoma dumosa.* This bed is in places rather indurated superficially, and forms projecting ledges.....	10 to 15

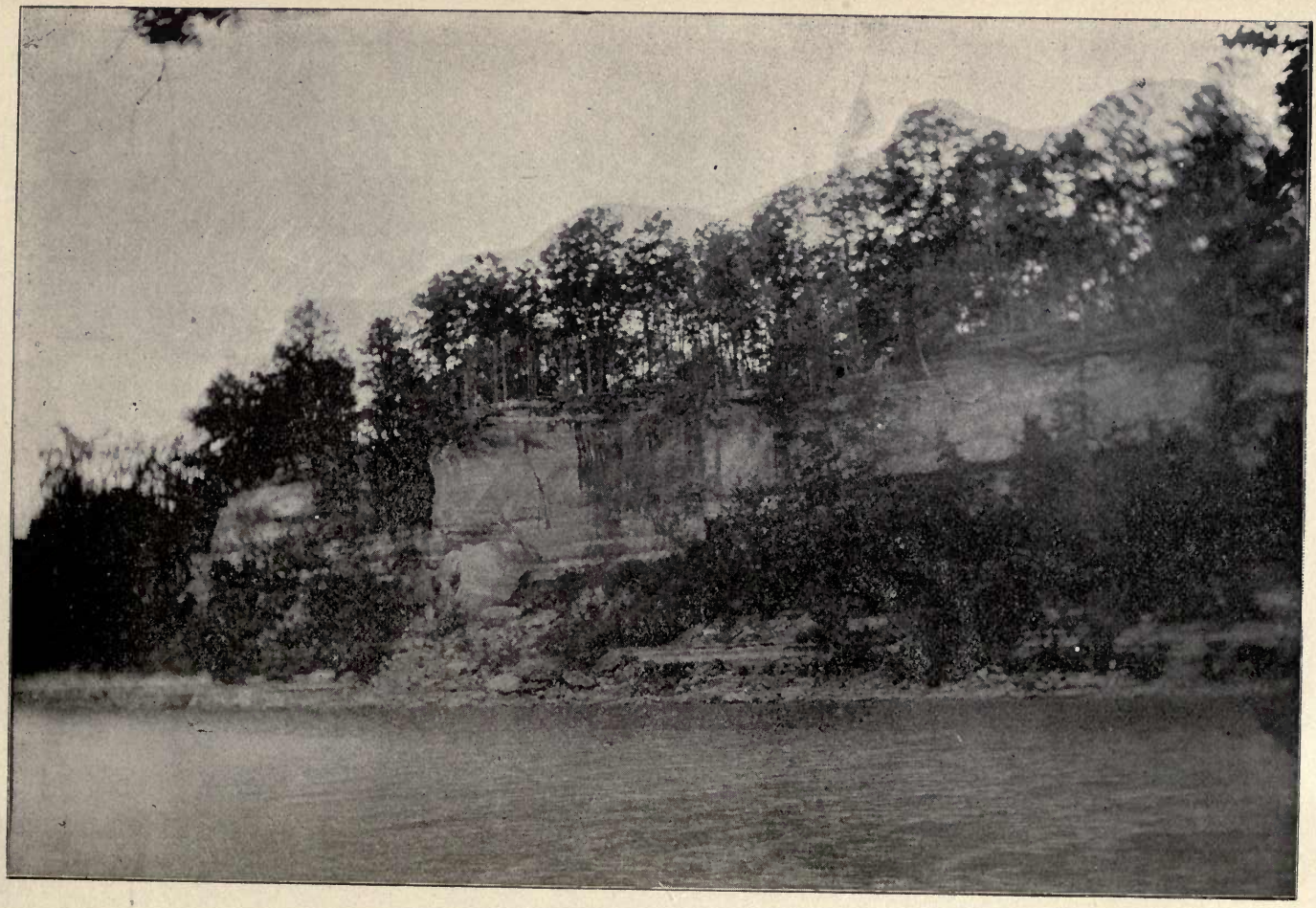

Plate XVI.—St. Stephens Bluff, Tombigbee River.

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5. Bluish clayey marl with much green sand, containing the same fossils as No. 4. It washes or caves out from under No. 4, which overhangs it..... 4 to 5
6. Massive joint clay, yellow on exposed surface, blue when freshly broken; no fossils observed. Extends below the water level to unknown depth; exposed ..... 3 to 4

The rock of this formation, which seems to be the best suited for cement material, is the soft "chimney rock" or orbitoidal limestone of bed No. 3 above. This usually quarried for chimneys and other constructions by sawing it out and dressing it down with a plane into blocks of suitable size, which are then laid like brick.

The numerous analyses given below will show that this rock is a purer limestone than most of the material of the Selma chalk of the Cretaceous formation above considered. In cement making it will, in consequence, require a larger proportion of clay to be mixed with it, and the question of obtaining suitable clay in sufficient quantity and in close proximity becomes one of some importance. The residual clay left after decomposition and leaching of the limestone seems to be fairly well adapted to the purpose. Besides this residual clay some analyses have been made of the clays of the river and creek bottoms of the country near the limestone outcrops, and of the clays of the Grand Gulf formation, which very generally in this section overlies the limestone. Some analyses of the last named clays have been made from material occurring near St. Stephens, and near Manistee Junction on the Repton Branch of the Louisville and Nashville Railroad. At this last-named locality the clay is present in sufficient quantity to be of value if the composition is suitable.

Details of Localities.

St. Stephens.—The first locality to be considered is the bluff at St. Stephens, a section of which has been given, and it may be taken as a typical section of the formation everywhere. At St. Stephens the whole of the soft orbitiordal limestone or "chimney rock" might be used, as the composition is uniform throughout. The overlying harder limestone has almost the same composition, but it is less easily crushed and handled. It may be quarried here from the surface down, as it is covered only by a thin layer of residual clay. The characters of the limestone and of the clay from here are sufficiently well shown

by the subjoined analyses (No. 1 of Table F, and 5 and 6, Table G.) The character of the clay of Grand Gulf formation near St. Stephens is shown in analysis No. 8 of Table G.

Below St. Stephens there is deep water to Mobile, with the exception of one bar, which may be removed without much trouble or expense.

Oven Bluff.—From Hobson's quarry, just above the Lower Salt Works Landing, down to Oven Bluff, a distance of 2 miles, the orbitoidal limestone or chimney rock occurs at the base of bluffs of Tertiary age.

At the quarry the hard limestone, which is being taken up for riprap work, lies ,as at St. Stephens, just above the soft chimney rock. Along the stretch of river above described this chimney rock is seen in a bed 15 to 20 feet in thickness, just above the river bottom, and is easily accessible. Analysis 2, Table F, of a sample from Oven Bluff will show the quality of the limestone here. As regards clay three varieties have been examined, a residual clay from over the limestone, a swamp-bottom clay from the low grounds of Leatherwood Leatherwood Creek, and clay from strata of the Grand Gulf formation which here overlies the St. Stephens limestone. The analyses of these clays have not yet been made.

The first shoal in the river above Mobile is a few miles above Oven Bluff, so that from this place down there is a 9-foot channel at all seasons, which will give to Oven Bluff a certain advantage over other localities in regard to transportation. The shoal mentioned is one which can be removed, so that St. Stephens may be classed with Oven Bluff as regards transportation by water, except that the former is some miles farther from the Gulf than the latter.

Analyses by Dr. Mallett of other specimens of this chimney rock are here presented. No. 8, Table F, is of a specimen from Colonel Darrington's place, in the lower part of Clarke county near Gainestown, and 9 and 10 are from other localities in Clarke county near the rivers.

Localities along the line of the Southern Railway.—At Glendon station, a few miles east of Jackson, there is an exposure of the chimney rock close to the track. The rock here is about 20 feet thick, and the limestone is covered by a bed of red residual clay similar to that at St. Stephens and Oven Bluff. The same chimney rock may be seen along the road between the sta-

tion and Jackson, and no doubt it occurs from Glendon up to Suggsville station, within convenient reach of the railroad. At Suggsville station the same rock occurs along the road leading from station to the town. This place is within a short distance of the railroad.

Between Suggsville and Gosport, the country rock is the St. Stephens limestone, but no particular attention was given to it for the reason that no railroad crosses the county along this line.

Along Alabama River.—At Perdue Hill the St. Stephens rock outcrops near the base of the hills which descend to the terrace on which the town of Claiborne stands. The bluff at Caliborne Landing shows near the summit the calcareous clay or clayey limestone which lies at the base of the St. Stephens formation, and which is generally thought to be the equivalent of the Jackson group of the Mississippi geologists. It is quite possible that this rock, where it occurs in sufficient quantity, may be suitable for cement making,, since it has a composition not far different from much of the Rotten limestone or Selma chalk. No investigations have yet been made concerning it, for the reason that there are comparatively few points where it appears in adequate thickness and in favorable localities as regards transportation.

At Marshall's Landing, just above the mouth of Randon's Creek, is the first exposure of the chimney rock along Alabama River. This occurs at the top of the bluff. It has the usual covering of residual clay, and the analyses presented (3 of Table F, and 7 of Table G,) will show the composition of the two. Below the orbitoidal or chimney rock at Marshall's there are 20 feet or more of a porous limestone, the analysis of which is given in Table F, No. 4. In the same bluff there are beds of calcareous clay which might possibly be used in mixing with the limestone. At the landing these would be difficult to quarry because of overlying strata, but they would certainly be found without cover along the bluffs above Marshall's if they should prove of value.

From Marshall's down to Gainestown Landing the river bluffs show beds of the limestone at numerous points. At Gainestown, the topmost bed of the St. Stephens, the hard crystalline limestone occurs not far above the water level in the river. This stone has been cut and polished and proves to be

a first-rate marble, inasmuch as it takes a good polish and shows agreeable variations in color. The soft chimney rock underlies the hard limestone here as at other points.

At Choctaw Bluff, some miles below Gainestown, there is the last exposure of the Tertiary limestones on the river. The material is an argillaceous limestone with numerous fossils, but it seems hardly likely to be of use in cement making.

Between Alabama River and the main line of the Louisville and Nashville Railroad.—A few miles east of Marshall's Landing, at Manistee Mills, the terminus of a sawmill road, there is a quarry of the chimney rock, conveniently situated as to transportation, since it is on the railroad. Across the country to the Repton Branch of the Louisville and Nashville Railroad, the St. Stephens limestone may, of course, be found at thousands of places, but no mention is made of these occurrences where they do not lie on railroad line.

Below Monroe Station, near Drewry on the Repton Branch, this road crosses the line of outcrop of the chimney rock, which at a number of points in the vicinity of Drewry lies within easy reach of transportation.

A few miles below Drewry, at Manistee Junction, there is a fine exposure of Grand Gulf clays in railroad cuts, both north and south of the station.

Analysis is given (No. 9 of Table G), of the clays from these cuts, from which their suitability from admixture with the limestone may be determined.

On the main line of the Louisville and Nashville Railroad.—The chimney rock may be found at many points below Evergreen in the vicinity of Sparta and Castleberry stations. There are many bluffs of this rock on the banks of Murder Creek in this vicinity, and there are several quarries from which the stone has been obtained for building purposes, within short distance of the railroad line. At the foot of Taliaferro's Heights the limestone forms high bluffs on the creek; at Ellis Williams Spring there are bluffs with the soft rock at the base and the hard horse-bone rock at the top, and on the creek bank, a few hundred yards away, is one of the quarries mentioned above. In fact the localities where the rock may be found within convenient distance of the railroad, and in a position favorable to

cheap quarrying, are numerous in all this region. No clays were seen except the usual residual clays from the decomposition of the limestone and a clay occurring close to Evergreen in the pits of Wild Brothers. Analyses 5, 6 and 7 of Table F, will show sufficiently well the character of the limestone in this section.

The Evergreen occurrences have attracted attention because of their location on the line of a great railroad system within short distance of tide water.

Farther to the east this limestone formation extends across Alabama and into Georgia and Florida, but as there is no north-south railroad east of the Louisville and Nashville at this time, the investigations have gone no further.

To summarize: While the St. Stephens limestone outcrops across the State from the Mississippi line to the Chattahoochee River, often occupying broad belts, attention has been concentrated on those localities which lie upon navigable streams or upon railroad lines terminating in Gulf ports. As compared with the Demopolis division of the Selma chalk, this limestone is more uniform in composition, higher in lime content, softer and more easily quarried and crushed, and in geographical position many miles nearer the Gulf.

Its thickness, on the other hand, is much less, although sufficient to supply an indefinite number of manufactories with raw material for cement.

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Table F.

Analyses of Tertiary Limestones.

Locality.	Silica.	Iron and aluminum oxides.	Calcium carbonate.	Magnesium carbonate.	Sulphuric anhydride.	Water and organic matter.
1 St. Stephens orbitoidal limestone, St. Stephens, Tombigbee river; R. S. Hodges, analyst	2.28	2.04	92.85	1.92	.13	.....
2 Orbitoidal limestone, "Chimney Rock," Oven Bluff, Tombigbee river; R. S. Hodges	4.18	3.26	89.32	2.38	.15	.81
3 Orbitoidal limestone, Marshall's Landing, Alabama river, Monroe county; R. S. Hodges	2.52	1.50	94.07	1.90	.08	.....
4 Limestone underlying the orbitoidal rock, Marshall's Landing; R. S. Hodges	11.44	3.34	80.46	3.09	.15	1.52
5 Chimney Rock, Taliaferro's Heights, near Evergreen, Conecuh county; R. S. Hodges	2.84	2.16	91.31	1.83	.07	1.79
6 St. Stephens orbitoidal limestone, near Evergreen; Dr. W. B. Phillips, analyst	1.26	1.72	96.09	.65	.02	.65
7 Orbitoidal limestone near Evergreen; D. W. B. Phillips	2.75	2.73	93.31	.23	.02	.60
8 St. Stephens orbitoidal limestone, Col. Darrington's, near Oven Bluff, Clarke co; Dr. J. W. Mallet	1.69	2.12	94.84	.96	.....	.....
9 St. Stephens orbitoidal limestone, Clarke co. near river; Dr. J. W. Mallet, analyst	2.44	.27	94.85	.....	.....	.....
10 St. Stephens orbitoidal limestone, Clarke county near river; Dr. J. W. Mallet, analyst	4.15	1.29	93.19	1.09	.....	.....

Table G.

Analyses of Clays (Cretaceous and Teritary) and Cement.

Number of anaylsis.	Silica.	Iron and aluminum oxides.	Calcium oxide.	Magnesium oxide.	Sulphuric anhydride.	Total sulphur.	Ignition.
1 Residual clay over limestone, at Demopolis Cement Works; R. S. Hodges, analyst	55.64	26.25	.91	1.97	Tr	....	13.90
2 Residual clay over limestone at P. H. Pitts' Home Place, Uniontown; R. S. Hodges	69.57	19.04	37	.....	.....	....	9.68
3 Residual clay, Graveyard Hill, Morgan Place, Uniontown; R. S. Hodges	56.74	28.10	.70	1.27	Tr	....	13.80
4 Residual clay, Reid Place, White Bluff, Alabama river, Dallas co.; R. S. Hodges	56.90	27.71	.86	1.64	.09	....	11.26
5 Residual clay over orbitoidal limestone, St. Stephens, Washington county; R. S. Hodges	59.71	24.79	.37	.....	.....	....	14.96
6 Residual clay over limestone, St. Stephens Bluff; R. S. Hodges	44.94	36.36	5.14	1.20	.....	....	13.77
7 Residual clay over limestone at Marshall's Landing, Alabama river, Monroe county; F. W. Miller, analyst	51.30	33.22	1.37	.96	.41	....	9.42
8 Grand Gulf clay, west of St. Stephens, Washington co.; R. S. Hodges	60.68	25.60	.48	.38	Tr.	....	9.92
9 Grand Gulf clay, Manistee Junc., Monroe county; F. W. Miller, analyst	66.60	25.86	.34	.34	.89	....	5.11
10 Cement manufactured by Alabama Portland Cement Co., Demoppolis; A. W. Dow, U. S. inspector of asphalts and cements, analyst.	20.25	13.44	63.60	1.03	.41	0.99	.....
11 Cement manufactured by Alabama Portland Cement Co., Demopolis; analysis from T. G. Cairns, general manager	19.99	13.74	61.36	.61	.....	....	.....
12 Cement manufactured by Alabama Portland Cement Co., Demopolis; R. S. Hodges, analyst	19.99	13.63	63.82	.83	1.16	....	.....

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